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Bachelor in Chemical and Biochemical Engineering

Thermochemical conversion of lignocellulosic biomass with the use of heterogeneous catalysts

Dissertation submitted in partial fulfilment of the requirements for the degree of Master in Chemical and Biochemical Engineering

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Para a minha família, a quem devo tudo..

An expert is a man who has made all the mistakes which can be made, in a narrow field
— Niels Bohr

Finish each day and be done with it. You have done what you could. Some blunders and absurdities no doubt crept in; forget them as soon as you can. Tomorrow is a new day. You shall begin it serenely and with too high a spirit to be encumbered with your old nonsense.

— Ralph Waldo Emerson

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Abstract

The utilization of biomass for production of chemicals, materials and fuels has been intensively investigated in recent years. γ-Valerolactone (GVL) is one of the important platform molecules that can be obtained from lignocellulosic feedstock. GVL has drawn an increasing attention thanks to its interesting properties which make it suitable for several applications. However, the real challenge is to synthesize γ-valerolactone directly from biomass in a one-pot process of hydrolytic hydrogenation.

Hydrolysis of biomass is conducted in the presence of mineral acid such as sulphuric acid (H_2SO_4) which is one of the problem for the catalyst performance. One of the solutions is a neutralization or separation of sulphuric acid from the mixture containing levulinic acid.

This work is devoted to study the catalytic performance of ruthenium catalyst in hydrolytic hydrogenation of different wood such as pine, poplar, beech and birch towards γ-valerolactone (GVL). The reactions were performed in two steps, the first was hydrolysis of biomass samples and further hydrogenation of formed hydrolysis products. Quantitative and qualitative analyses of the produced liquors were made by high-performance liquid chromatography. The properties of different biomass samples were characterized by X-ray diffraction (XRD), Fourier Transmission Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy (SEM). The characterization of the surface properties of the investigated catalyst was performed by Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) and Temperature-Programmed Reduction (TPR).

The results showed that the reaction performance depends on several factors, such as pH which strongly influence the γ-valerolactone yield. The activity of the catalyst was influenced by the presence of impurities or carbon deposit, which was proved by ToF-SIMS and TPR.

Keywords: Ruthenium catalyst, γ-valerolactone, biomass conversion, levulinic acid hydrogenation

Resumo

A utilização de biomassa para a produção de químicos, materiais e combustíveis tem sido intensamente investigada nos últimos anos. γ-Valerolactona é uma das importantes moléculas de plataforma que pode ser obtida a partir de matérias-primas lignocelulósicas. GVL tem atraído cada vez mais atenção graças às suas interessantes propriedades que a torna adequada para várias aplicações. No entanto, o verdadeiro desafio consiste em sintetizar γ-valerolactona diretamente da biomassa num processo de "one-pot" de hidrogenação hidrolítica.

A hidrólise de biomassa é conduzida na presença de ácidos minerais como o ácido sulfúrico (H_2SO_4), que representa um dos problemas para a performance catalítica. Uma das soluções é a neutralização ou a separação de ácido sulfúrico a partir da mistura que contem acido levulínico.

Este trabalho é dedicado ao estudo da performance catalítica do catalisador de ruténio na hidrogenação hidrolítica de diferentes tipos de madeira como o pinho, álamo, faia e bétula para obter γ-valerolactona (GVL). As reações foram realizadas em dois passos, o primeiro correspondeu à hidrolise das amostras de biomassa e o segundo à hidrogenação dos produtos formados na hidrólise. As analises quantitativas e qualitativas dos produtos líquidos foram realizadas por cromatografia líquida de alta performance. As propriedades das diferentes amostras de biomassa foram caracterizadas por Difração de Raio X (XRD), Espectroscopia de Infravermelho por Transformada de Fourier (FTIR) e por *Scanning Electron Microscopy* (SEM). A caracterização da superfície do catalisador foi realizada por *Time-of-Flight Secondary Ion Mass Spectrometry* (TOF-SIMS) e Redução de Temperatura Programada (TPR).

Os resultados mostraram que as condições ótimas de reação dependem de vários fatores como o pH, que fortemente influenciou a produção de γ-valerolactona. A atividade do catalisador foi influenciada pela presença de impurezas ou deposito de carbono, que foi provado por ToF-SIMS e por TPR.

Palavras chave: catalisador de ruténio**,** γ-valerolactona, conversão de biomassa, ácido levulínico, hidrogenação

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Introduction

Since the industrial revolution, energetic supply has improved tremendously and it has been the basis for the global development. However, this development has been sustained by fossil fuels such as oil, natural gas and coal, thus making it the world's leading source of energy [1] [2].

In addition, the demand for energy is increasing at an exponential rate due to the world's population growth. According to the United Nations (2007) the global population will increase by 30 percent in the next 40 years going from 7 billion people in 2012 to more than 9 billion in 2050 and if the current consumption path is kept, the use of fossil fuels will grow exponentially, causing the decline and disappearance of known fossil fuel resources [3] [4].

On the other hand, there are other factors behind the use of fossil such as political, social, environmental. Among them, it is environmental factor and its problems associated with the use of fossil fuels that present the biggest problem.

Production of energy from fossil fuels involves the emission of greenhouse gases such as carbon dioxide (CO_2) into the atmosphere. CO_2 and other greenhouse gases act like a blanket, absorbing IR radiation and preventing it from escaping into outer space [5]. As a consequence, their presence leads to the gradual heating of the earth known as global warming.

Global warming causes significant climate change such as: the rise in sea levels; increasing ocean acidification; extreme weather events and other severe natural and societal impacts [6]. Therefore, it makes sense for global warming to be controlled and for this reason, several legislations were created to control CO_2 emissions and the emergence of 'Green Chemistry'.

Green Chemistry is defined as: *'The utilisation of a set of principles that reduces or eliminates the use or generation of hazardous substances in the design, manufacture and application of chemical products.'* based on the definition proposed by Anastas and Warner (Green Chemistry: Theory and Practice, P T Anastas and J C Warner, Oxford University Press, Oxford, 1998) [7].

According to Anastas and Warner's definition, twelve principles of chemistry were created in order to development alternative sustainable technologies. Their implementation is not a solution but shows the way to reduce the environmental impact of the use of fossil fuels and one of the means to achieve this is the use of sustainable feedstock. Thus, is in this context that the concept of biorefinery emerges and consequently, biomass.

1.1 Biorefinery

The concept of biorefinery is not completely new, having appeared at the beginning of this century. More recently, with the recognition of the potential of bioeconomy for the sustainable development associated with economic growth, biorefineries have become increasingly important worldwide through the recognition of the many economic, environmental and social benefits they can bring to societies [8].

Thus, the term biorefineries is widely discussed and there are several definitions for it.

According to the American National Renewable Energy Laboratory, biorefinery "is *a cluster of bio-based industries* producing chemicals, fuels, power, products, and materials". Biorefineries are also defined as "sustainable processing of biomass into a spectrum of marketable products and energy" by IEA BIOENERGY. The main difference between these two concepts is that the former includes industries as part of biorefineries and the latter also includes the processes. A third definition was presented by Demirbas being very quoted since it demonstrates the role of biorefineries today, " the biorefinery concept is analogous to today's crude oil refinery, which produce multiple fuels and products from petroleum" [8].

In general, a biorefinery facility seeks the sustainable use of biomass for the simultaneous production of energy, materials and chemicals, preferably with added value. Then, there will be products with a great volume and low economic unit value (such as biofuels), and there will also be small volume products with high added value (such as chemical specialties, additives, etc.) [9] [10] (Figure 1.1).

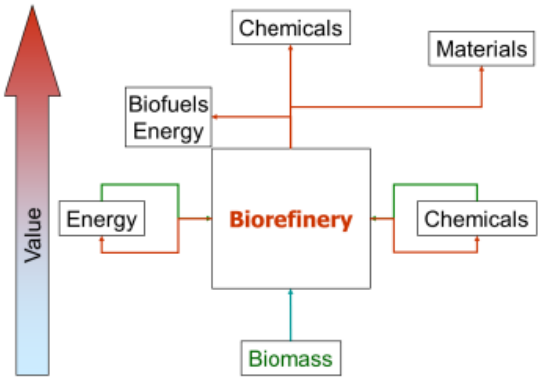

Figure 1.1. Biorefinery concept [10].

Biorefineries can be classified according to the type of platform used, the types of products to be produced, the raw material and conversion processes [11]:

- The platforms (e.g., C_5/C_6 sugars, syngas, and biogas) are intermediates connecting different biorefinery systems and their processes. The number of involved platforms is an indication of the system complexity.
- The two biorefinery product groups are energy (e.g., bioethanol, biodiesel, and synthetic biofuels) and products (e.g., chemicals, materials, food and feed).
- The two main feedstock groups are 'energy crops' from agriculture (e.g., starch crops, short rotation forestry) and 'biomass residues' from agriculture, forestry, trade and industry (e.g., straw, bark, wood chips from forest residues, used cooking oils, waste streams from biomass processing).
- The four main conversion processes are biochemical (e.g., fermentation, enzymatic conversion), thermochemical (e.g., gasification, pyrolysis), chemical (e.g., acid hydrolysis, synthesis, esterification) and mechanical processes (e.g., fractionation, pressing, size reduction)
- Although biorefineries have advantages, such as the use of renewable sources, to compete with well-established chemical (petro) industries, biorefineries need to combine innovation and development efforts by promoting rapid transposition to a larger scale.

1.2 Biomass

Biomass is the only sustainable source of organic compounds as equivalent to petroleum to produce fuels, chemicals and materials.

Although fossil fuels are still ahead of the demand for raw materials to produce energy and materials, biomass currently covers approximately 10 percent of the global energy supplies, of which two thirds is used in developing countries for cooking and heating (Figure 1.2) [12].

In 2009, about 13 percent of the biomass consumption was used to produce heat and energy, while the industrial sector consumed 15 percent and the transportation 4 percent. The main countries that use biomass as a source to produce energy were: Brazil, the USA and India. Brazil leads the list with 18 percent of total industrial use in 2009. The USA and India each had 16 percent of the use of biomass for the industry. Nigeria, Canada, Thailand and Indonesia each held about 4 percent of global participation in the same year [12].

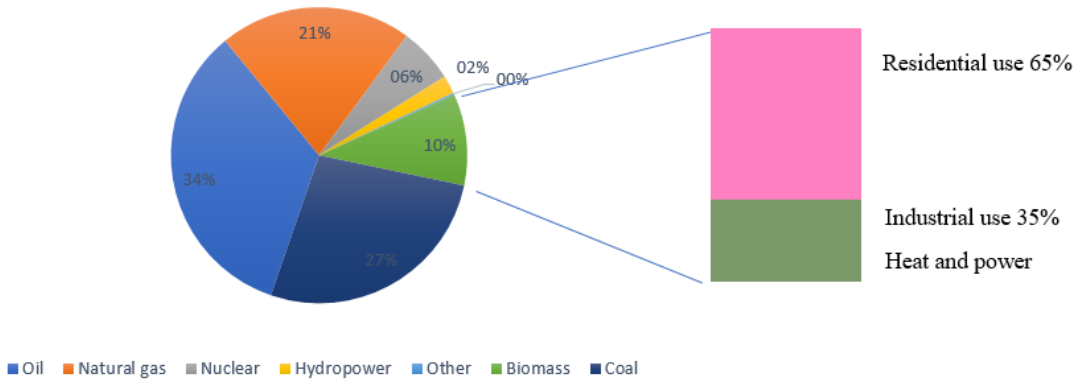

Figure 1.2 Share of energy sources in the world (2013) [12].

The term biomass is used to describe all biologically produced matter and can be divided into first, second and third generation.

The first generation biomasses are produced directly by photosynthesis and are taken directly from the land. They include perennial short-rotation woody crops and herbaceous crops, the seeds of oil crops, and residues resulting from the harvesting of agricultural crops and forest trees (e.g., wheat straw, corn stover, and the tops, limbs, and bark from trees).

The biomass for second generation include wood, organic waste, food waste and specific biomass crops. They result from the processing of primary biomass resources either physically (e.g., the production of sawdust in mills), chemically (e.g., black liquor from pulping processes),

or biologically (e.g., manure production by animals). In addition, the process to produce 2nd generation fuels are more complex than 1st generation biofuels because it requires pre-treating the biomass to release the trapped sugars. This requires more energy and materials. Third generation biomasses use specially engineered crops such as algae as the energy source. These algae are grown and harvested to extract oil within them. The oil can then be converted into biodiesel through a similar process as 1st generation biofuels, or it can be refined into other fuels as replacements to petroleum-based fuels [13] - [15].

In fact, it can be considered three general classes of feedstocks derived from biomass: starchy (including sugars), triglyceride, and lignocellulosic. Among them, Lignocellulosic is the most abundant, inexpensive and can be considered as second generation biomass [16].

1.2.1 Lignocellulosic Biomass

Lignocellulosic biomass is one of the most abundant renewable resource on Earth and is a principal feedstock to produce biofuels and valuable chemicals. It is a mixture of complex sugars and lignin, a non-carbohydrate polymer that provides strength and structure to plant cell walls [17] [18]. Lignocellulosic biomass also contains a smaller amount of pectins, proteins, inorganic compounds and extractives. Extractives consist of organic and inorganic compound, for example, soluble non- structural materials such as non-structural sugars, nitrogenous material, chlorophyll, and waxes [19]. The amount of these compounds and type of extractives present are dependent of biomass source.

Typically, lignocellulosic materials consist mainly of three polymers: lignin (15-20%), hemicellulose (25-35%), and cellulose (40-50%). The structures are illustrated in Figure 1.3 for wood.

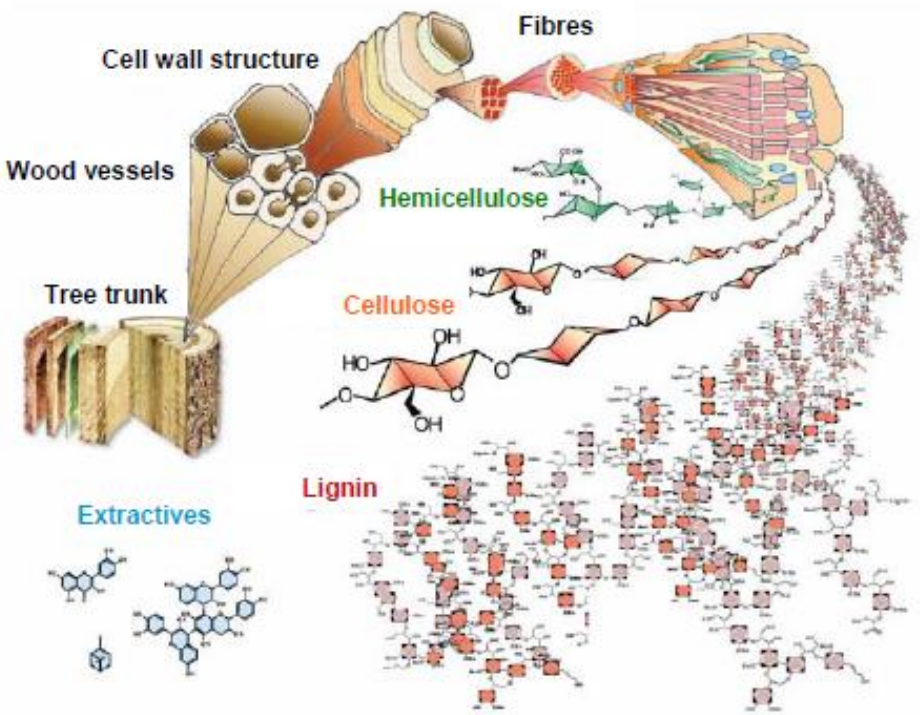

Figure 1.3. Illustration of lignocellulosic biomass structure from wood.

The amount of the three components and type of bond depend on their source, may vary from species to species as well as across different parts in the same plant [20] and can be also influenced by harvest time and how it was cultivated Table 1.1.

Wood as a lignocellulosic source material has many advantages. One of the most important is its abundance and an existing infrastructure for harvesting, processing and handling [21].

There are three major types of this type of lignocellulosic biomass: softwood, hardwood and grasses, which contain promising candidates for future biorefinery feedstocks.

Table 1.1 Cellulose, Hemicellulose and Lignin in Softwood, Hardwood and grasses [19].

Biomass	Lignin (%)	Hemicellulose (%)	Cellulose (%)
Softwood	25-35	25-35	45-50
Hardwood	18-25	24-40	40-55
Grasses	12	31.4	45

Softwoods are considered one of the most important commercial trees because of their properties such as, fast-growing and height. In general, softwood has a largely uniform microscope structure, which origin from the high abundance of single cell type (called-tracheids), which are narrow, trick-walled cell type. Moreover, this type of wood is the most recalcitrant feedstock type. Softwoods contain more lignin than those three types of plants [22]. Combined with high guaiacyl to syringyl ratio in the lignin which is considered to be the reason for its higher resistance to delignification compare to grasses or hardwoods biomass. Therefore, harsher conditions are usually required and strong nucleophiles such as sulphide (S^{2-}, in Kraft pulping) or sulphite (HSO_3^-) ions are added to facilitate removal of lignin and prevent lignin recondensation. The main hemicellulose sugar in softwood is mannose, followed by xylose. An example of softwood are pine, fir, spruce and birch [23].

Willows, poplar and beech are examples of hardwood biorefinery crops. Hardwoods have more complex structure than softwoods and contain large water-conducting pores or vessels that are surrounded by narrower fibre cells. They consist in more lignin and hemicellulose than grasses. The lignin is made up of of guaiacyl and syringyl units and the main hemicellulose sugar is not mannose but xylose [23].

In respect to grasses, they are usually, of all feedstock, the least resistant to deconstruction. Grasses have a distinctively different pore structure compared to trees. The amount of hemicellulose and lignin are lower in comparison with softwood and hardwood. The major hemicellulose sugar is xylose and lignin has more diversified composition than the hardwoods, followed by softwoods [23].

Generally, the accessibility of the fibers of grasses is larger and beneficial for the reduction of the digestibility of these biomasses under conditions of low severity.

The varying chemical composition and structural differences between the lignocellulose types affects their amenability to deconstruction, therefore the effects of each lignocellulose deconstruction method should be assessed according to the feedstocks [23].

Lignin

Lignin is the most complex natural polymer, conferring impermeability and structural support to plants. It is an amorphous three-dimensional polymer with phenylpropane units as the predominant building blocks. These units are three monolignol precursor: coniferyl alcohol, sinapyl alcohol and p-coumaryl alcohol [18]. Once incorporated into the lignin polymer, the subunits are identified by their aromatic ring structure and therefore called guaiacyl, syringyl and

p-hydroxyphenyl subunits, respectively. Figure 1.4, represents a chemical structure of the three monolignols involved in the lignin structure

The lignin polymer contains a wide range of linkages. The most common linkage is the β-O-4 ether bond. Roughly 50% of all inter-subunit bonds are of this type. The β-O-4 ether bonds lead to a linear elongation of the polymer. Other C–O and C–C linkages are present in lower abundance, and branching occurs when lignification is advanced [23].

The structure of lignin depends on many factors and in particular the source of biomass as can be seen in Table 1.1. This difference in composition has a great effect to remove lignin from woody tissue (as by natural enzymatic or industrial chemical processes) and therefore on biomass deconstruction [23].

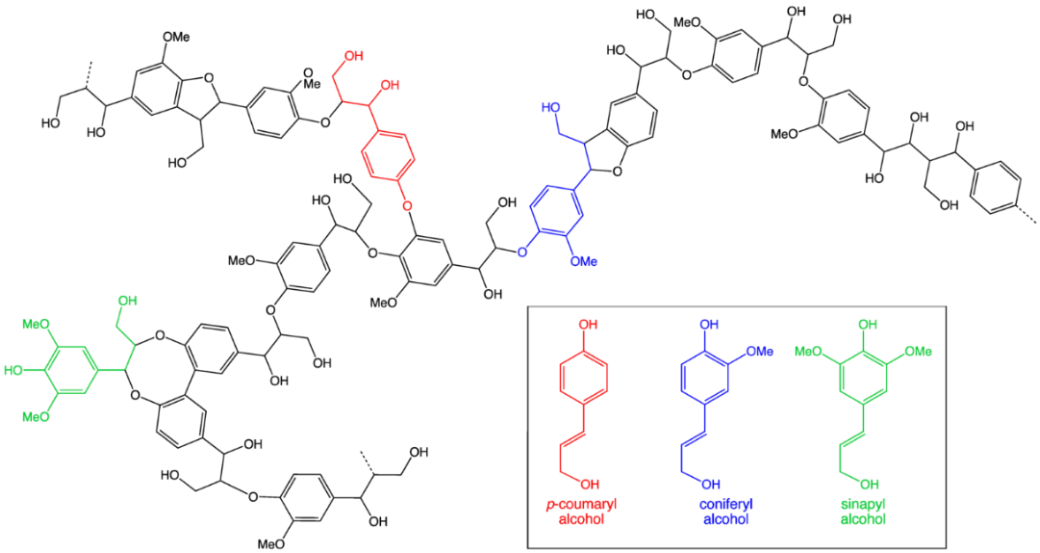

Figure 1.4 General structure of lignin and the chemical structure of the three monolignols [25].

Lignin represents a great potential in different industries, for example, it is being used to produce fertilizers, as well as in bioplastics. Also, carbon fibers obtained from lignin are used to make high-energy super capacitors as energy storage devices.

Hemicellulose

Hemicelluloses are heterogeneous polysaccharides, Figure 1.5 which are located mainly in the secondary cell walls, and together with cellulose and lignin, they build up the structure of

the plants in a way that generates the best combination of mechanical support and transport properties [24]- [26].

The general structure of hemicellulose is based on various sugar units formed by pentoses (C_5) and hexoses (C_6), depending on the type of plants, being classified as xylans (β-1,4-linked L-xylose units), mannans (β-1,4-linked D-mannose units), arabinans (α-1,5-linked D-arabinose units) and galactans (β-1,3-linked D-galactose units). Other sugars such as L-rhamnose and L-fucose may also be present in small amounts [24].

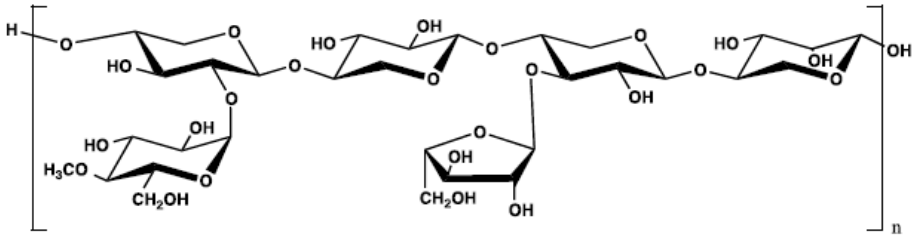

Figure 1.5 Structure of Hemicellulose [25].

Moreover, this feature renders it partially soluble in water at elevated temperatures, and the presence of an acid helps to improve its solubility.

The applications for hemicellulose are present, for example, in pharmaceuticals such as filler material for tablets, cholesterol reducing agent, dietary fiber and leukemia cytotoxicity. Other applications include barrier materials for food packaging or biopolymers with new properties [26].

Cellulose

Cellulose is the most common polysaccharide and it is the main cell wall polymer that supports the plant [27].

Structurally, cellulose is a linear polymer consisting solely of glucose units to form repeating units of cellobiose. The chemical formula of cellulose is $(C_6H_{10}O_5)n$ and the structure of one chain of the polymer is presented in Figure 1.6.

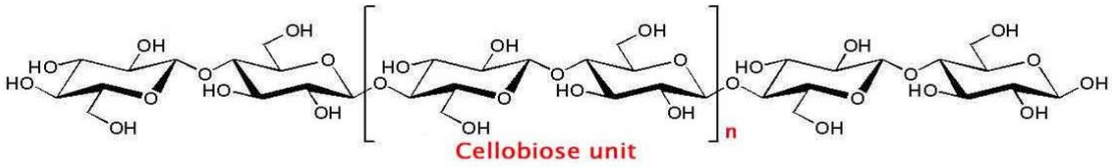

Figure 1.6 Structure of Cellulose [66].

The glucose units are linked by (1→4)-β-D-glycosidic bonds allowing the polymer to be arranged in long straight chains. The bond between other chain of celluloses is made by hydrogen bonding and Van der Waals forces which are responsible for its chemical stability, structure rigidity, and tensile strength [28].

Within these cellulose fibrils there are regions where the cellulose chains are arranged in a highly ordered (crystalline) structure, and regions that are disordered (amorphous-like) (Figure 1.7)

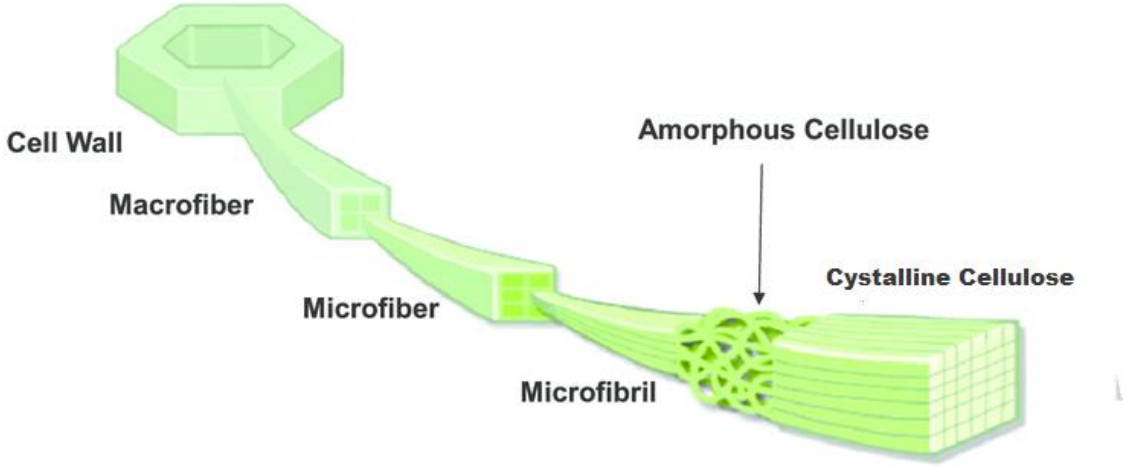

Figure 1.7 Schematic of cellulose microfibril showing one of the suggested configurations of the crystalline and amorphous regions [67].

Crystalline structure comprises the major proportion of cellulose and it is created when the coalescence of several polymer chains leads to the formation of microfibrils, which in turn are united to form fibrils and consequently cellulose fibers [18]. In contrast, a small percentage of unorganized cellulose chains form is non-crystalline or amorphous cellulose which lead to cellulose to be more susceptible to enzymatic degradation in its amorphous form [19].

At a macro level, cellulose forms the cell walls of a plant in close association with hemicellulose and lignin.

Currently, seven polymorphs of cellulose (Iα, Iβ, II, III_I, III_{II}, IV_I, V_{II}) are known.

Cellulose Iα and Iβ are forms found in nature. Form Iα is abundant in the cell wall of some algae and in bacterial cellulose, while cellulose Iβ is predominant in cotton, wood, and ramie fibers. Cellulose Iα and Iβ can be found in the same sample and along the same microfibril. Cellulose I is the crystalline cellulose that is naturally produced by a variety of organisms (trees, plants, tunicates, algae, and bacteria), it is sometimes referred to as ‘‘native’’ cellulose. Its structure is thermodynamically metastable and can be converted to either cellulose II or III [28]. Cellulose II is obtained either by regeneration of dissolved cellulose or by a process called mercerization. This process consists of swelling native cellulose fibers in a solution of concentrated sodium hydroxide, followed by the removal of the swelling agent. Cellulose III can be obtained from cellulose I or II by the ammonia fiber explosion process (AFEX), resulting in cellulose III_I and III_{II}, respectively. Treating cellulose III_I and III_{II} in glycerol at 206ºC affords cellulose IV_I and IV_{II}, respectively. However, the most of the crystallographic studies are focused on cellulose I and II, both because of its natural occurrence and its industrial importance, respectively [29].

Many properties of this compound depend on its degree of polymerization (DP), i.e. the number of glucose units that make up one polymer molecule [30]. Commonly, DP can be between 800-10000, depending on cellulose source and treatment of the raw material [31].

In contrast to monomer (glucose) and short oligomers, cellulose is not soluble in water and has a poor ability to absorb water [32]. Reasons for this are the high molecular weight of this compound (solubility is usually inversely related to polymer length) and the comparatively low flexibility of cellulose polymer chains. Moreover, the intermolecular hydrogen-bonding, and the hydrophobic flat top and bottom surfaces enabling van der Waals interactions between sheets, allow intimate and ordered packing of cellulose strands and contribute to the insolubility of polymer in water and most solvents [23].

However, cellulose is soluble in concentrated acids, but severe degradation of the polymer by hydrolysis is caused.

It should be noted that also deconstruction of cellulose is strongly affected by the DP. The reduction in the DP of cellulose depending on type of pre-treatment, for example, after acidic and basic pre-treatments, the DP of poplar cellulose was reduced by ~86% and ~20% respectively [31].

Cellulose has numerous applications, but the production of ethanol, platform chemicals such as levulinic acid (LA) and 5-hydroxymethylfurfural (HMF) being one of the most promising [33] - [35]as can be seen ahead in this chapter.

1.2.2 Lignocellulosic biomass pretreatment

Pretreatment consists of a process to break down cellulose, hemicellulose and lignin structure into their corresponding monomers. During this process, the compact structure of lignocellulosic is disrupted and cellulose fiber is exposed [36]. This step is the first and most important in lignocellulosic biomass processing. It is the key by which the lignocellulosic biomass could be modified so as to make it suitable to further processes or reactions in order to convert it into valuable products [37]. However, the resistant and complex structure of lignocellulosic materials makes their pretreatment not simple either [38]. The crystallinity of cellulose, and the presence of covalent bonds represent the main problem. Lignin also, is a big barrier for the hydrolysis of cellulose.

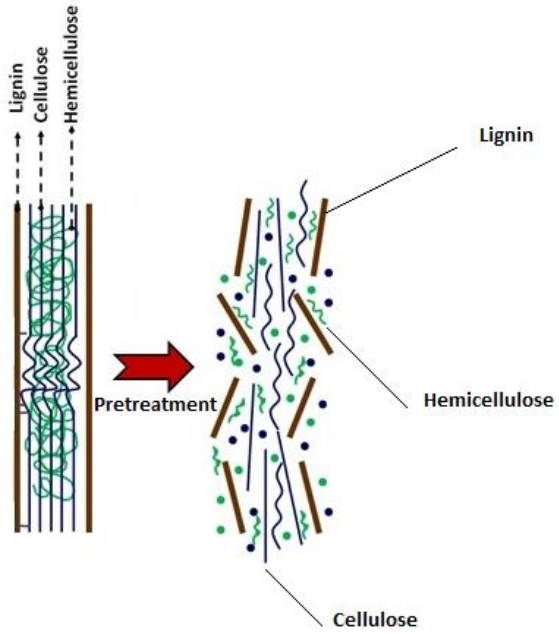

Figure 1.8 Representation of pretreatment effect in lignocellulosic biomass(Adapted [68]).

The identification of the lignocellulosic structures allows the selection of the pretreatment method. The selection of the method takes into account the raw materials, enzymes and organisms to be applied, general economic evaluation and environmental impact.

Pretreatment must meet the following requirements [22]:

- Dissolve and reduce the crystallinity of cellulose by breaking the hydrophobic interactions among the glucoses, as well as the hydrogen bonds that bind the monomers;
- Totally or partially separate lignin from cellulose and hemicellulose by cleaving the α or β-arylether, methoxyl group and carbon-lignin bonds;
- Reduce the polymerization, alter the structure or redistribute the lignin on the cell wall;
- Depolymerize or dissolve the hemicellulose by removing the acetyl groups, glycosides or uranic esters that are present in their respective structures;
- Chemically modify the carbohydrates;
- Increase the surface area and porosity and reduce the thickness, volume, particle size and the presence of vascular beams in the cell wall and break bonds.

Basically, the pretreatment should increase the permeability of the reagent carbohydrates of the vegetable cell walls, however each method works differently in the physicochemical deconstruction of lignocellulosic structures resulting in different yields and products [22] [38].

Pretreatment methods can be divided into different categories: biological, physiochemical, physical and chemical as shown in Table 1.2.

Table 1.2 Different methods for biomass pretreatment [26] [36] [39] [40]

Pretreatment	Process	Means	Effect
Biological	Microorganisms	Fungi and actinomycetes	Delignification and reduction in degree of polymerization of cellulose.
Physiochemical	Explosion (steam, ammonia fiber, AFEX, CO_2, SO_2)	High-pressure	Decrease of cellulose crystallinity and DP and increase accessible of the surface area and pore size; partial or complete delignification and hydrolysis of hemicellulose
Physical	Mechanical comminution	Combination of chipping, grinding and/or milling	Reduction of cellulose crystallinity
	Pyrolysis	Temperatures higher than 300ºC	Decomposition of cellulose to gaseous products and residual char
Chemical	Ozonolysis	Ozone treatment	Remove lignin and hemicellulose
	Acid Hydrolysis	Concentrated acids (e.g. H_2SO_4, HCl, HF…	Decrease of cellulose crystallinity and DP and partial or complete degradation of hemicellulose
	Alkaline Hydrolysis	Sodium, potassium, calcium and ammonium hydroxides	Rupture of lignin structure; decrease of cellulose crystallinity and DP, cleavage of glycosidic bonds
	Oxidative delignification	Peroxidase enzyme with presence of H_2O_2	Dissolution of lignin and hemicellulose
	Organosolv process	Organic or aqueous organic solvent mixture with inorganic acid catalysts (HCl or H_2SO_4)	Cleavage of linkage between hemicellulose and lignin

On the other hand, biomass fractionation is a difficult process and has contributed to the high cost of processes utilizing lignocellulosic feedstocks. Typically, its isolation proceeds through pretreatment followed by hydrolysis, which represent one of the main challenges in the utilization of lignocellulosic biomass for the production of sugars. Therefore, nowadays an active area of research is the optimization of biomass pretreatment and hydrolysis to improve the suitability of this feedstock.

However, among the numerous conversion technologies developed for biomass exploitation, hydrolysis is a method that converts carbohydrates into their building blocks, i.e. sugars [41].

1.2.3 Valorisation of lignocellulosic biomass

Hydrolysis pathways are essential for lignocellulose processing if higher selectivity is required in biomass utilization, such as, in the production of chemical intermediates or hydrocarbons for transportation fuel.

The majority of the selected platform chemicals are derived from the cellulose and hemicellulose fraction of lignocellulosic biomass [41].

The key to success in the production of these platform chemicals is to choose the right biomass as the raw material and to use each of its components at its maximum value.

Independently of whether the goal is to produce liquid fuels or commodity chemicals, the first step consists to depolymerise and (partially) deoxygenate the lignocellulose, which the selective transformations require isolation of sugar monomers. This step is one of the most complex and expensive for lignocellulosic feedstocks. In addition, during the primary conversion of lignocellulosic biomass, some residual protein is also formed, which the amount of each product depends on its source

Once hemicellulose and cellulose are isolated they can be hydrolytically converted into their constituent building blocks (Figure 1.9): C_5 and C_6 monosaccharides respectively.

The conversion of these feedstocks into valuable products can be envisaged by subsequent transformations of a set of biomass derivative molecules, the so-called platform molecules [16].

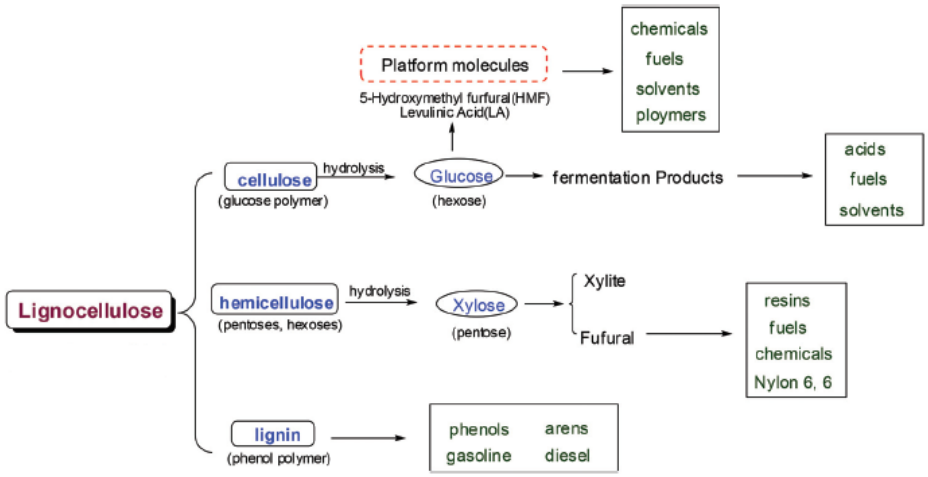

Figure 1.9 Valorisation of lignocellulosic biomass.

1.3 Hydrolysis of cellulose

After isolation from the rest of components of lignocellulosic biomass, cellulose can be converted into its monomer, glucose. This process called hydrolysis or depolymerisation (Figure 1.10). However, cellulose hydrolysis is limited by its crystalline structure because of the glycosidic bonds. Hydrolysis of cellulose can be achieved enzymatically (more selective) or chemically (lower cost). In this process the β-1,4-glycosidic bonds of the polymer is broken and opened the possibility of subsequent catalytic transformations. It is considered an essential step for the conversion of cellulose [42].

The acid-catalysed hydrolysis of cellulose typically involves a mineral acid catalyst, however at concentrations greater than those used for hemicellulose deconstruction.

After converted to glucose, several chemicals such as gluconic acid (oxidation), sorbitol (hydrogenation), H_2 (aqueous phase reforming), polyols (hydrogenolysis), and furans (hydrolysis), can be obtained by different routes. On the other hand, as an alternative, cellulose can be processed in aqueous solution containing a dilute acid at higher temperature to convert the cellulose into equimolar amounts of levulinic and formic acids, passing through glucose and HMF as intermediates. In that case, two common approaches are used: one approach uses high mineral acid concentrations at low temperatures (e.g. 323 K), and the other approach uses dilute mineral acid solutions at higher operating temperatures (423–513 K). The dilute acid approach is typically favoured due to the lower acid concentrations being less corrosive on equipment and lower acid costs [42].

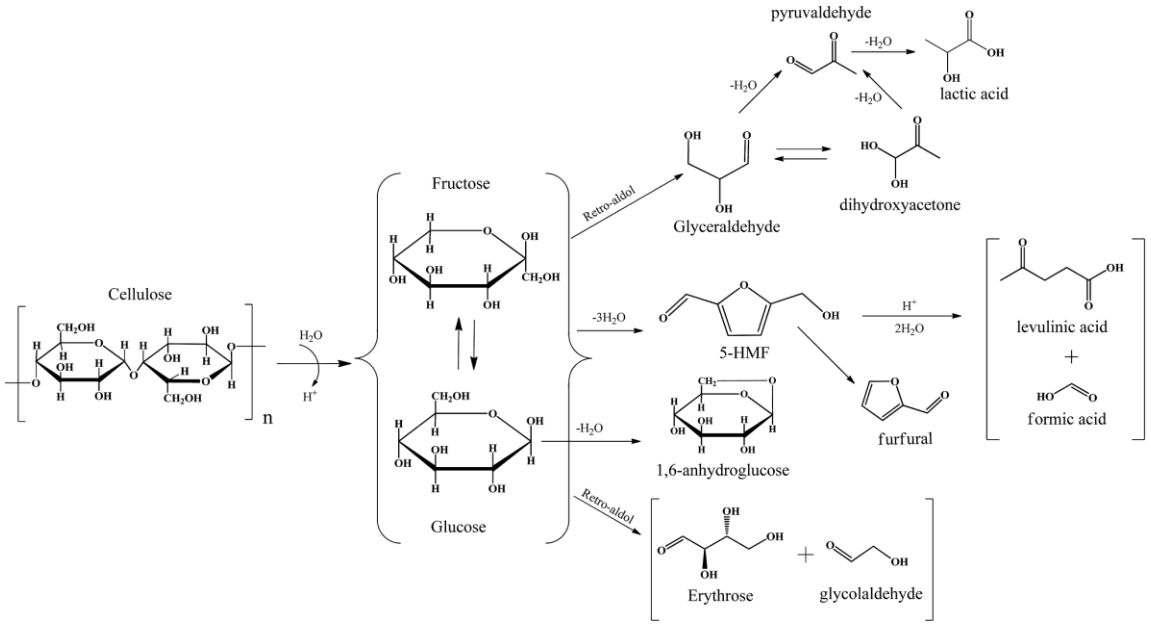

Figure 1.10 Illustration of cellulose depolymerisation [69].

1.4. Platform molecules

Initially, the selection of platform molecules was made by the US Department of Energy (DOE) in 2004 and revised by Bozell and Petersen. The selection was made on the basis of several indicators such as, availability of commercial technologies for its production and their potential to be simultaneously transformed into fuels and chemicals in biorefineries facilities. Therefore, on the list of platform molecules include sugars (glucose, xylose), polyols (sorbitol, xylitol, glycerol), furans (furfural, 5-hydroxymethylfurfural) and acids (succinic, levulinic, formic, lactic acids) [16] [41].

In comparison with molecules which are produced from fossil feedstocks, platform molecules are already functionalized compounds. This advantage allows transforming them into valuable chemicals without a higher number of steps than required starting from fossil fuels.

Several applications are associated to the platform molecules. Production into liquid hydrocarbon fuels by catalytic transformation of these molecules appears an interesting approach for the production of advanced biofuels.

However, platform molecules are highly oxygenated compounds and their conversion into liquid hydrocarbon fuels requires oxygen removal reactions (i.e. dehydration, hydrogenolysis, hydrogenation, decarbonylation/ decarboxylation, etc.) and in some cases in combination with the adjustment of the molecular weight via C–C coupling reactions (e.g. aldol-

condensation, ketonization, oligomerization) of reactive intermediates. These C–C coupling reactions are especially important when starting from biomass derivatives with C_5–C_6 carbons (derived from monosacharides) and the final products are hydrocarbon fuels to be used in diesel engines (C_{10}–C_{20}) and jets (C_9–C_{16}) [41].

Another interesting application of platform molecules is their transformation into fuels additives (gasoline/diesel gasoline), which are chemical compounds that are added to fuels to accomplish a several functions such as helping to maintain the cleanliness of engine parts, temper fuel gelling and nozzle choking, prevent corrosion and incomplete combustion of the fuel, improve fuel economy and reduce greenhouse gas and particulate emissions [41].

The present thesis focuses on the hydrodeoxygenation of levulinic acid (LA) as a biomass-derived platform molecule to γ-valerolactone (GVL).

Levulinic acid (LA)

One of the most important compound in the selected list of platform molecules is levulinic acid (4-oxopentanoic acid) which can be upgraded to several valuable compounds by different routes (Figure 1.11). Levulinic acid (LA) has been proposed as such a versatile building block containing a ketone carbonyl group and an acidic carboxyl group, which can be used for preparation of various high-value organic chemicals, polymers, components of flavouring and fragrance industry, textile dyes, extenders for fuels, antifreeze products, antimicrobial agents, herbicides and also plasticizers and fuel additives with numerous potential industrial applications [43].

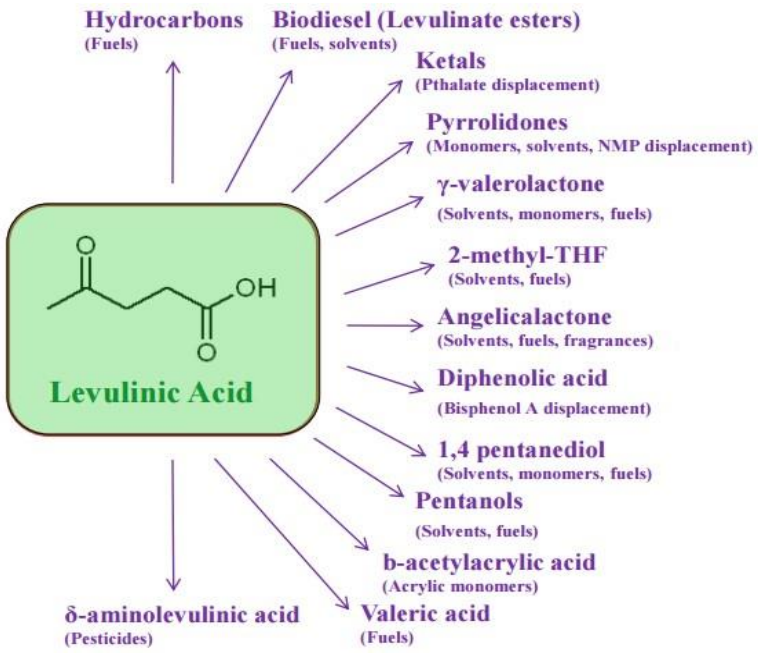

Figure 1.11 Levulinic acid structure and its applications [70].

Levulinic acid is formed by two main routes (Figure 1.12)

One of them, LA is produced via cellulose hydrolysis and dehydration to hydroxymethylfufural (HMF), which upon subsequent hydration produces levulinic acid, equimolar amounts of formic acid along with large amounts of humic acids or humins, black insoluble materials, which are produced by unwanted polymerization reactions. A second route consists pentoses such as xylose, the main component of hemicellulose fraction, can be converted to levulinic acid. In this case the process involves the dehydration of xylose to furfural, subsequent hydrogenation to furfuryl alcohol which is finally hydrolysed to levulinic acid [44].

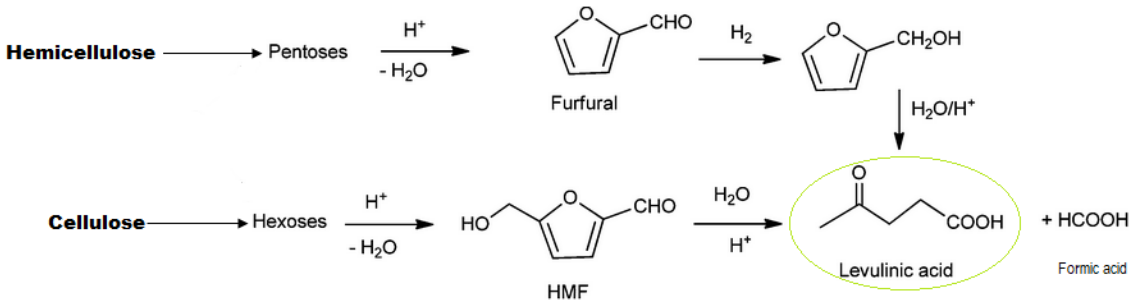

Figure 1.12 Possible mechanisms of levulinic acid production (Adapted) [16].

Beside Levulinic acid, γ-valerolactone (GVL) issued from the transformation of lignocellulosic biomass has been attracted significant attention. In the case of GVL synthesis, transfer hydrogenation, which formic acid (FA) can be used as an internal hydrogen source in LA hydrogenation into GVL [34] (Figure 1.13)

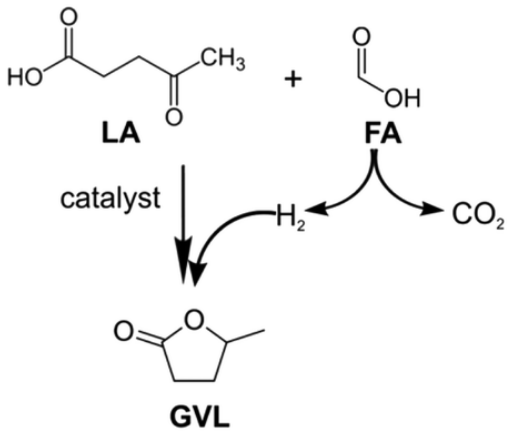

Figure 1.13 Levulinic acid hydrogenation with formic acid decomposition as an internal hydrogen source towards GVL [34].

Formic acid (FA)

Formic acid (systematic called methanoic acid) (Figure 1.14) is the simplest carboxylic acid and an important intermediate in chemical synthesis. Among carboxylic acids, formic acid is distinguished by its acid strength, its failure to form an anhydride, and its reactivity as a reducing agent, which results from a property due to the CHO group.

The chemical formula is HCOOH [45].

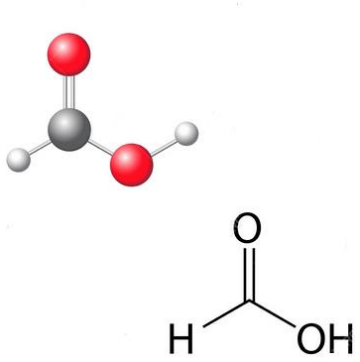

Figure 1.14 Chemical structure of formic acid [71].

Relatively to the applications, formic acid (FA) as the hydrogen storage materials has been proposed based on a sustainable energy storage cycle between formic acid and carbon dioxide. In that case, energy of cycle can be released in the form of hydrogen gas, which can occur either in a direct formic acid fuel cell or during formic acid decomposition.

Decomposition of formic acid consists of two reaction pathways: dehydrogenation (1) to form H_2 and CO_2, and dehydration (2) to form H_2O and CO. On the other hand, under harsh reaction condition the water-gas-shift (3) can take place as well as the Fischer–Tropsch reaction from the CO and CO_2 products in the presence of catalyst (4) and (5). CO_2 can also be reduced into CH_4 through the Sabatier reaction in which CO can be formed as the by-product. Although less often mentioned, the formation of formaldehyde is possible due to the reaction of formate ions ($HCOO^-$) (6) [34].

$$HCOOH \rightarrow H_2 + CO_2 \ (1)$$

$$HCOOH \rightarrow H_2O + CO \ (2)$$

$$CO + H_2O \rightarrow H_2 + CO_2 \ (3)$$

$$CO + 3H_2O \rightarrow CH_4 + H_2O \ (4)$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \ (5)$$

$$2HCOOH \rightarrow HCHO + CO_2 + H_2O \ (6)$$

Beside of hydrogen storage the use of formic acid as an internal hydrogen source has been investigated for the synthesis of GVL from LA. This process is interesting because formic acid is a stoichiometric side-product in the conversion of (ligno)cellulose into LA (Figure 1.12) and in the presence of selective catalyst, FA decomposes into CO_2 and H_2, which can be used as an internal hydrogen source in the LA hydrogenation into GVL (Figure 1.13). Therefore, the reaction pathway strongly depends on the catalyst used [34].

γ-Valerolactone (GVL)

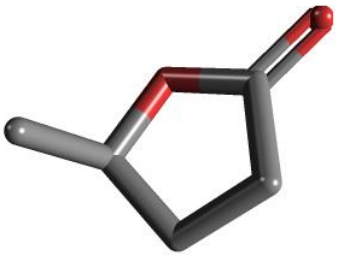

Figure 1.15 Structure of γ-valerolactone (GVL) [72].

γ-Valerolactone (GVL) is a five carbon (Valero) cyclic ester with five atoms (4 carbons and 1 oxygen) in the ring (γ-lactone). GVL is a colourless liquid and safe to store and move globally in large quantities, because it has low melting, high boiling and flash points and definite smell which makes it suitable for the production of perfumes and food additives. It is also stable under air and miscible with water, assisting biodegradation [46]. The properties of GVL make reactive enough to produce several specialty chemicals (e.g. butene, valeric acid, and 5-nonanone) as well as synthetic fuels as depicted in Figure 1.10. An example is MTHF, which is an important compound formed by GVL hydrogenated for production of fuel additives. On the other hand, GVL can be also used directly as a liquid fuel or as an additive to current petroleum fuels.

Alternatively, GVL is proposed as a platform for the production of jet fuels (C_8+ alkanes) or diesel fuels (C_9-C_{18}) alkanes [47].

Besides fuels several strategies have been proposed to convert GVL into interesting monomers to make polymers similar to those derived from petroleum but with different chemical properties. In addition, GVL also shows interesting solvent properties and is hence proposed as green solvents or as precursor for other green solvents [16] [47].

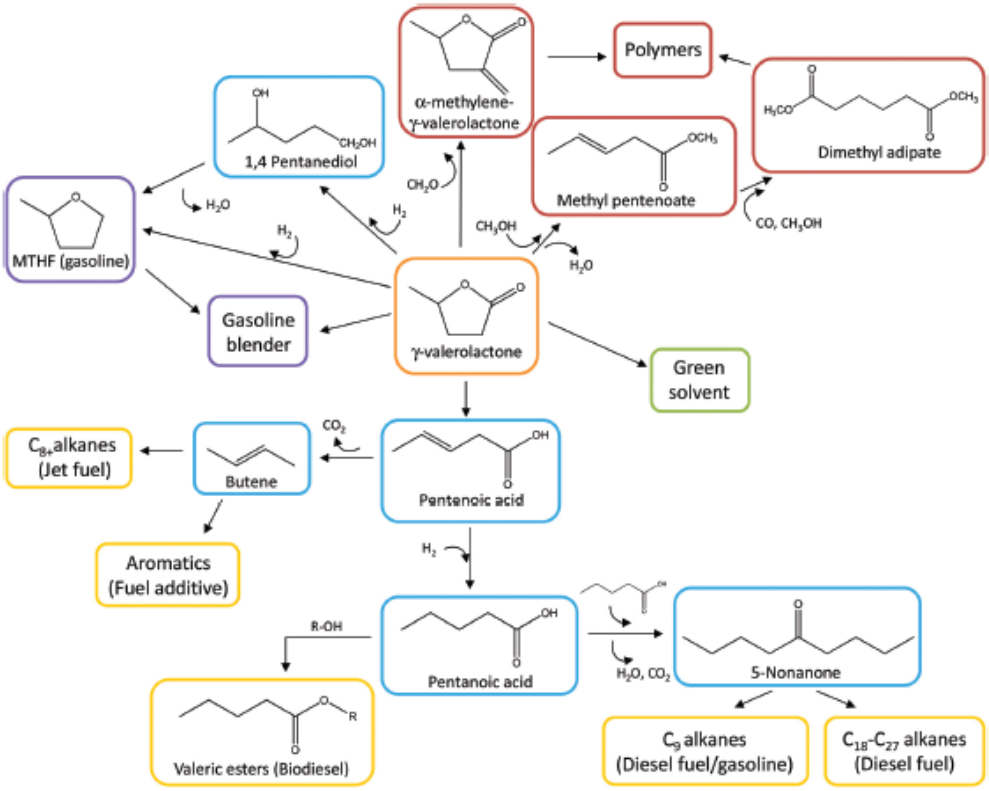

Figure 1.16 GVL applications [44].

1.4 Levulinic acid hydrogenation to produce GVL

GVL is formed by hydrogenation of levulinic acid via main two routes (Figure 1.17).

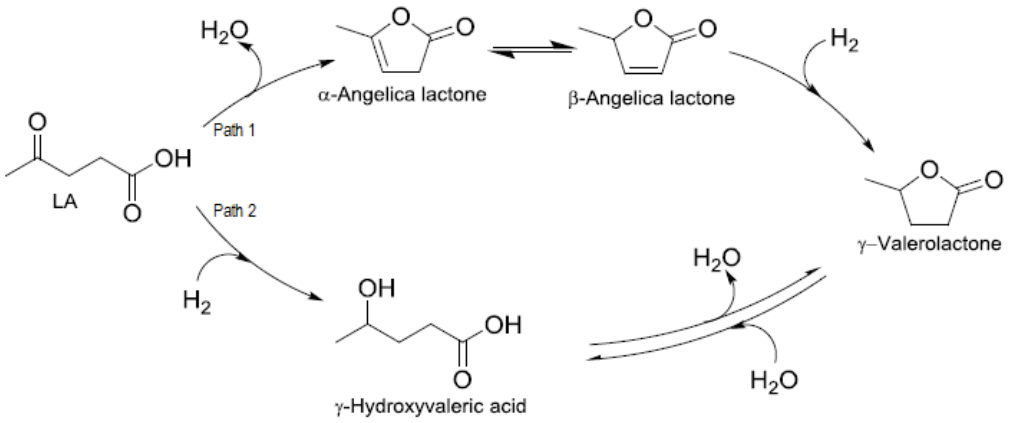

Figure 1.17 Two possible routes of GVL production: path 1 LA dehydration; path 2- LA hydrogenation (Adapted [47]).

One of them involves the hydrogenation of levulinic acid towards γ-hydroxyvaleric acid, an unstable intermediate, which undergoes spontaneous lactonization rendering γ-valerolactone. A second route LA is dehydrated to α-angelica lactone (which occurs in equilibrium with β-angelica lactone), and is then hydrogenated to GVL, however in this case yields of GVL are lower since acidic media promotes the polymerization of angelica lactone and formation of coke.

LA hydrogenation to GVL is a catalytic process. For this reason, several different catalysts have been developed in recent years [16].

1.5 Catalyst

Catalyst is defined as a substrate which transforms reactants into products, through an uninterrupted and repeated cycle of elementary steps in which the catalyst participates while being regenerated to its original form at the end of each cycle during its lifetime [48].

In the hydrogenation of levulinic acid (LA) into γ-valerolactone (GVL) has been performed using heterogeneous and homogeneous metal catalyst.

A typically heterogeneous catalyst is a solid material and the catalytic reaction generally occurs on a solid surface. A main advantage of these catalyst is that they are in a solid phase and can easily be separated and recycled from the reactants and products, because the catalyst is in a separate phase than reactants. In contrast, in case of homogeneous catalyst, it is difficult to separate and recycle.

On the other hand, heterogeneous catalyst in levulinic acid hydrogenation is usually less active and required high temperature and pressure compared to homogeneous catalyst. However, because of the complexity of separation of homogeneous catalyst from the reactor mixture, the heterogeneous catalysts are preferable in industry [48].

Therefore, numerous studies of heterogeneous catalyst were reported for implementation of LA hydrogenation to GVL. Wrigth and Palkovits reported different methods of producing GVL from levulinic acid using mainly heterogeneous catalysts [16] [49].

Many noble metals such as Ru, Pd, Pt, Ni, Rh, Ir, Au on different supports e.g. organic (activated carbon) and inorganic (alumina, titania, silica etc..) has been performed in a wide range of solvents. Recently TiO_2 and ZrO_2 have been found to be efficient supports catalyst in this reaction because of their acid-base properties [16] [44] [50] [51].

Among them, Ru and Pd catalysts showed high performance in LA hydrogenation [51].

However, Ru based catalysts being the most commonly used because it demonstrated to be active just not for hydrogenation of levulinic acid (LA) but also to the decomposition of formic (FA) acid [16] and it is the central focus of this thesis.

Ruthenium catalyst

Ruthenium supported by carbon is a monometallic catalyst which has shown high performance for levulinic acid hydrogenation to GVL.

The activity of the Ru catalyst depends on the reaction media, so the selection of an appropriate solvent is very important [35].

Many studies show Ru on a carbon support in various solvents, such as methanol, ethanol, 1-butanol, 1,4- dioxane, tetrahydrofuran (THF), water and mixtures: ethanol-water, methanol-water or without any solvent and excellent yields of GVL have been reported [51]- [55].

Recently, Palkovits et al. reported that in the presence of Ru catalysts water raises an amount of GVL produced. In that case 86% of GVL yield was observed while in presence of ethanol (61%) as a reaction medium [54].

It was explained by the fact that the presence of a H-bonded water molecule dramatically reduces the energetic span of the preferred reaction pathway for the hydrogenation of LA, consequently improving the catalytic activity. This behaviour can be assigned to oxophilic metals, such as Ru and also Ni or Co [54].

It was also demonstrated that the particle size and degree of dispersion of the catalytically active phase have significant role in increasing of the GVL yield.

Therefore, activity of Ru catalyst is determined by such factors as pore size, crystal size mechanical strength, presence of modifiers, etc.

In fact, ruthenium supported on carbon is a highly selective catalyst for hydrogenation of levulinic acid. The mechanism was proposed by Liguori et al. (Figure 1.18).

It was proposed that in a first step H_2 and LA are chemisorbed on the Ru surface, followed by the heterolytic cleavage of the H-H bond and the transfer of one hydrogen to an intermediate species stabilized by the interaction with Ru.

Transfer of the second H atom results in the formation of Ru-bonded, which rapidly dehydrates to GVL [56].

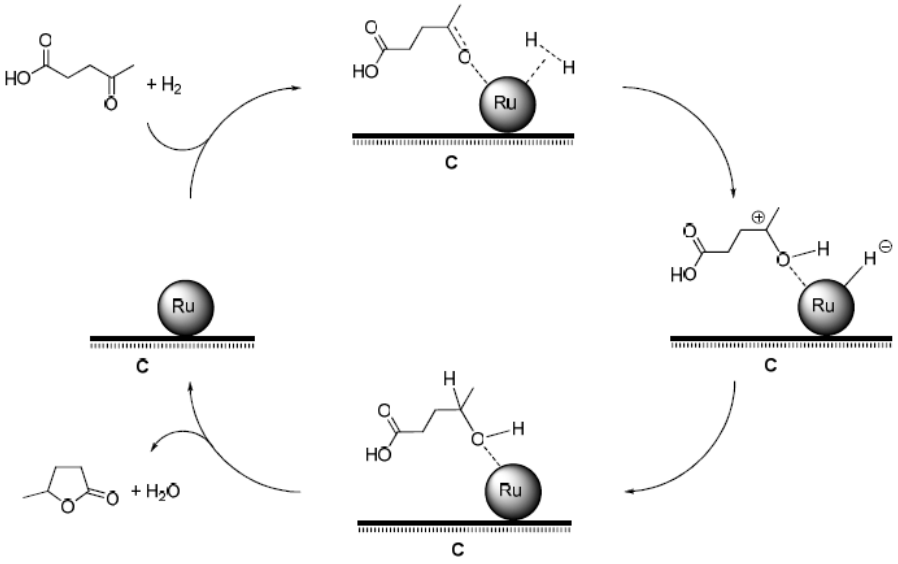

Figure 1.18 Mechanism of levulinic acid hydrogenation on Ru/C catalyst [56].

In the case of formic acid decomposition, it was also showed by theoretical calculations that formic acid can easily and strongly adsorb dissociatively on Ru when is derived from the $RuCl_3$ precursor, which was showed to be more active in comparison with Ru/C derived from acetylacetonate (acac) precursor [34].

On the other hand, Ru catalyst are not active only in the hydrogenation of pure levulinic acid to GVL but also in the reaction with real biomass feedstock [35]. However, it has been obtained lower yields.

1.6 Challenges in biomass conversion

Most studies reporting LA hydrogenation to produce GVL have employed pure, commercial LA or mixtures of commercial compounds that simulate the products that would be obtained from the hydrolysis of cellulose or lignocellulosic biomass (e.g., mixtures of LA and formic acid) [34] [41] [44] [50]- [56].

Moreover, they do not take into account the presence of mineral acids such as sulphuric acid which is commonly used in the hydrolysis of (ligno) cellulose biomass for production of GVL.

In fact, the synthesize of GVL directly from biomass (one-pot process hydrolytic hydrogenation) is a real challenge [51].

Starting from biomass, several compounds are present during the process which can influence the activity of the catalyst. It was demonstrated that in the hydrolysis, a greater number of side products can be formed which may also undergo hydrogenation (e.g. to hydroxymethylfurfural or sugar alcohols). In consequence, it can lead to the production of humins (coke) which can deactivate the catalysts used in the reaction. Moreover, the presence of mineral acid results in poisoning of the catalysts by sulphur and consequently in the decrease in GVL yield [35] [51].

In addition, it was proved that the presence of mineral acids present in the feed of levulinic acid can reduce the activity of ruthenium- catalyst by adsorption of sulphur. One of solutions is a neutralization or separation of mineral acid from the mixture containing LA by solvents like alkylphenol, as it was proposed by Alonso et al [44].

Other authors have proposed the use of heterogeneous catalysts (e.g., Amberlyst 70) for the initial reaction of cellulose or glucose to LA, which would eliminate the mineral acid all together.

Heterogeneous catalyst systems are beneficial since they eliminate the use of mineral acids from the process, which improves downstream processing. However, LA yields must be improved for heterogeneous catalysts to become viable for production of LA [44].

2

Objectives

The biomass conversion into particular molecules is considered one of crucial step in today's biorefinery schemes.

The aim of this work was the sustainable synthesis of GVL over ruthenium catalyst with the use of different types of wood. The prepared catalysts were submitted to activity tests in the mentioned process. Moreover, an analysis of their physic-chemical properties was performed

3

Experimental

3.1 Materials

In this work, different type of lignocellulosic biomass from wood, namely pine, beech, birch and poplar were tested. The samples were air-dried and prepared in the Institute of Papermaking and Printing, Lodz University of Technology (LUT). All the feedstock material was grinded with a knife mill to obtain smaller particles and stored in plastic containers at room temperature. Pure α-cellulose supplied by Sigma- Aldrich was also tested as a blank sample.

The solution of sulfuric acid 0.9% for acid hydrolysis of lignocellulosic materials was prepared by mixing with distilled water and sulfuric acid 95%(CHEMPUR - Poland).

The Ru/C catalyst was prepared from hydrated $RuCl_3$ supplied by Acros Organics 99% purity) on a high surface area C-DARCO® (Sigma-Aldrich) activated charcoal support. The Ru content in the Ru/C catalysts was obtained by inductively coupled plasma atomic emission spectroscopy (ICP-AES). The Ru wt% of the Ru/C catalysts was 5 ± 0.3%. The catalyst was stored in PFA samples containers at room temperature.

In catalyst tests the following reagents were used: distilled water, 0.9% H_2SO_4 and NaOH. NaOH aqueous solutions was prepared from mixing with distilled water and NaOH 98.8% supplied by CHEMPUR (Poland). Levulinic acid was obtained from Sigma-Aldrich (98% purity) and formic acid 85% was purchased from CHEMPUR (Poland).

In a typical levulinic acid (LA) hydrogenation experiment, the hydrogen (H_2) was supplied from Linde AG (Germany).

For the alkaline experiments, calcium carbonate ($CaCO_3$) (98.5% purity), calcium oxide (CaO) (96% purity) and calcium nitrate ($Ca(NO_3)_2{*}4H_20$) (98.5% purity) were tested. All the alkaline compounds were acquired from CHEMPUR (Poland). The pH paper purchased from Lach- Ner, s.r.o (Czech Republic) was used to control the pH. The reactions were made in a 100-ml stainless steel autoclave (Parr, USA) and in a stainless steel autoclave (Berghof, Germany), equipped with a Teflon insert allowing a reaction volume of 45 ml.

For high-performance liquid chromatography (HPLC) (Perlan) equipped with a refractive index detector and a Rezex ROA column. 0.005N sulphuric acid (H_2SO_4) was used as an eluent. All samples solutions were prepared using by HPLC water from Institute of General and Ecological Chemistry LUT.

For Fourier Transform Infrared Spectroscopy (FTIR), the KBr (≥ 99 % trace metals basis) supplied from Sigma- Aldrich was used to prepare the sample. The samples were mixed in agate mortar supplied by Sigma- Aldrich. Before measurements the mortar was cleaned with Diethyl Ether 99.5% (CHEMPUR – Poland). Liquid Nitrogen acquired from Linde AG (Germany) was used to cooled down the spectrometer MCT detector (77K).

For Temperature-Programmed reduction the mixture of 5%H_2 in Ar was used supplied from Linde AG (Germany).

For the Secondary ion mass spectrometry measurements, the pellets were prepared with silica obtained from Sigma- Aldrich. The same equipment from Fourier Transform Infrared Spectroscopy (FTIR) to prepare the pellet was used in this measurement.

3.2. Catalyst preparation

In this work ruthenium supported by carbon was the main catalyst and its preparation was carried out according to the procedure represented in Figure 3.1.

Figure 3.1 Illustration of the preparation of the Ru/C catalyst.

Ruthenium catalyst (with 5wt.% of metal) was prepared by incipient wet impregnation for 24h from 84.75 ml of hydrated $RuCl_3$ (Acros Organics) on 2.85g of activated charcoal as a support. After impregnation, the excess of solvent was evaporated under continuous stirring, and catalyst was dried at 120 ºC for 2h, and reduced before the reaction in hydrogen flow at 500ºC for 1h.

For comparison, 4%Ni-1%Au/Al_2O_3 and 5%Ru/10%Ca-TiO_2 catalyst were also tested. The preparation was carried out according to the literature [50].

3.2.1 Catalytic tests

Biomass materials/cellulose hydrolysis toward LA and subsequent hydrogenation toward GVL with FA as an internal source

In a typical experiment, 1 g of cellulose and 30 ml of aqueous acid solution (0.9 wt.% H_2SO_4) were combined in a 100-ml stainless steel autoclave from Parr. The reactor was heated to 170 ºC for 5 h. After the reaction, the reactor was cooled down to 40ºC and the solid components were separated from the reaction mixture. Then, catalyst was added (0.2 g) and reactor was heated to 190 ºC for 5 h.

Hydrogenation of Levulinic acid

In a typical experiment, 0.36 g of LA, 0.2 g of catalyst, and 26 ml of distilled water were combined in a 100-ml stainless steel autoclave from Parr. The reactor was pressurized with H_2 to 15 bar and the temperature was maintained at 190 °C for 1 h. At the end of the reaction, the reactor

was cooled down, the remaining pressure was released and the reaction mixture was centrifuged to separate the solid catalyst and the product solution.

Decomposition of Formic acid

In a typical experiment, 0.122 ml of formic acid (FA), 0.2 g of reduced catalyst, and 26 ml of distilled water were mixed in a 100-ml stainless-steel autoclave Parr. The reactor was then heated to 190 °C for 1 h. After 1h, the reactor was cooled down, the remaining pressure was released and the reaction mixture was centrifuged to separate the solid catalyst and the product solution.

LA hydrogenation with formic acid as a hydrogen source

In a typical LA hydrogenation experiment, 0.36 g of LA, 0.122 mL of FA, 0.2 g of a catalyst and 26 ml of water were mixed in a 100-ml stainless-steel autoclave Parr. The temperature was maintained at 190 °C for 2 or 5 h. At the end of the reaction the reactor was cooled down, the remaining pressure was released and the reaction mixture was centrifuged to separate the solid catalyst and the product solution.

Reaction product analysis

In all cases, after the end of the reaction, the reactor was cooled down, and the remaining pressure was released. The gaseous products were analysed by gas chromatography (VEB Chromatrom, Berlin).. The liquid products were analyzed by high performance liquid chromatography (Perlan). In the case of biomass hydrolysis, the calculations of products (levuninic acid (LA), Formic acid (FA) and γ-Valerolactone (GVL) were made based on cellulose content.

3.3 Methods

High performance liquid chromatography

The liquid components were analysed by high-performance liquid chromatography equipped with refractive index detector and Rezex ROA column (0.005N H_2SO_4 was used as an eluent). The conversion of LA and yield to GVL were estimated using equations presented below:

The conversion of (pure, and present in hydrolysis mixture) levulinic acid LA (XLA) was determined based on the amount of LA utilized in the reaction (mLA,0) (pure or present in mixture after hydrolysis reaction taking into consideration the amount detected using HPLC) and the amount of LA after reaction taking into consideration the amount detected using HPLC (mLA):

$$X_{LA} = [m_{LA;0} - mL_{LA}/m_{LA,0}] * 100$$

The yield to GVL obtained from cellulose YGVL, based on the definition:

$$Y_{GVL} = (n_{product}/n_{substrate}) * 100$$

where: $n_{substrate}$ equal to the molar amount of $C_6H_{10}O_5$ in the starting substrate, $n_{product}$ equal to the molar amount of the certain product as determined by HPLC.

The yield to GVL obtained from pure LA, Y_{GVL1}:

$$Y_{GVL1} = (n_{product1}/n_{substrate1}) * 100$$

where $n_{substrate1}$ equal to the molar amount of pure LA (starting substrate), $n_{product1}$ equal to the molar amount of the certain product as determined by HPLC.

Before measurement it was necessary to filtrate solutions in order to discard catalyst's residues. Then solution was diluted 10-times and 20 μL of solution was injected. REZEX ROA-Organic Acid column with polymer fulfilment (grain with sulfonic copolymer styrene – divinylbenzene) was used. Temperature inside column was 60°C. As an eluent 0,0025 M H_2SO_4 was used with flow of 0,6ml/min.

Gas Chromatography

Gaseous products were analysed by gas chromatography (VEB Chromatrom, Berlin). Measurement is based on movement analysed sample (in gaseous phase) by gas carrier towards

column the mixture of gases is separated. In the outlet of system is Thermal-Conductivity Detector (TCD). TCD allows to detect composition of analysed mixture in carried gas according to retention time, which in strictly defined for each chemical compound. During analyses argon was used as gas carrier with gas flow 15 ml/min, with sensitivity TCD detector 128. Each injection included 1 cm^3 volume of gaseous mixture.

3.3.1 Characterization techniques

SEM

Scanning Electron Microscopy (SEM) measurements were performed by S-4700 microscope (Hitachi, Japan) to image of samples using an acceleration voltage 20 kV, equipped with energy dispersive spectrometer (EDS) (Thermo Noran, USA). The samples were coated with Pt using a vacuum sputter-coater to improve the conductivity of the investigated materials.

FTIR

Fourier Transform Infrared Spectroscopy (4000-400 cm^{-1}) of cellulose and lignocellulosic biomass were recorded at room temperature in a DRIFTS cell using Nicolett 6700 spectrometer with MCT detector. Spectra were measured accumulating 64 scans at 4 cm^{-1} resolution. Some samples were prepared using the KBr technique for comparison. The pellets were prepared with mixing of 28.5 mg of KBr and 15 mg of wood materials. All samples were grinded in a mortar, until a homogenous mixture was obtained. After, the samples were pressed under 5 tons pressure.

XRD

Room temperature powder X-ray diffraction patterns were collected using a PANalytical X'Pert Pro MPD diffractometer in the Bragg–Brentano reflection geometry. Copper CuK radiation was use from a sealed tube. Data were collected in the 2θ range 4–50º with a step of 0.0167º and an exposure per step of 50 s. The samples were spun during data collection to minimize preferred orientation effects. A PANalytical X'Celerator detector based on Real Time Multiple Strip technology and capable of simultaneously measuring intensities in the 2θ range of 2.122º was used.

ToF-SIMS

Time-of-Flight Secondary Ion Mass Spectrometry is used to characterize surface of solid materials and allows to analyse composition and distribution of and ions on the surface of tested sample. TOF-SIMS is used to analyse surface of catalysts in order to check interactions between metal ions. Tests were carried on using Time of Flight Secondary Ion Mass Spectrometer TOF-SIMS IV Company ION-TOF, Germany. As a primary ion source is used ion beam Bi^{3+} amount around 3x 10^{10} ions/cm^2. The measurements were done in Institute of General and Ecological Chemistry of Lodz University of Technology. Before measurement samples were tabletting. Charge, which accumulates during measurement, is neutralized by flood gun – electron beam with low energy.

TPR

Temperature-Programmed Reduction (TPR) was performed on AMI1 system from Altamira Instruments, USA, equipped with a thermal conductivity detector and was used for examining the reducibility of catalysts. The mixture of 5 vol.% H_2 and 95 vol.% Ar with the space velocity at 30ml/min was used. TPR profiles were recorded from 30°C up to 600°C, with a heating rate of 10°C/min.

4

Results and Discussion

4.1 Characterization of the biomass samples

4.1.1 Composition of biomass

In this work, four different types of wood were studied. They were used as a feedstock for synthesis of levulinic acid (LA), formic acid (FA) and γ-valerolactone (GVL). Among them, one of the most interesting is GVL, which has drawn an increasing attention. γ-Valerolactone can be obtained from cellulose or sugars in several steps. The first step is hydrolysis of cellulose towards glucose which after subsequent dehydration is converted to hydroxymethylfurfural (HMF) and then to levulinic acid (LA) in the presence of acid catalyst. LA can further be hydrogenated towards GVL using metal catalyst [35].

The biomass feedstock besides cellulose consists of lignin and hemicellulose and also contains many other impurities and heavy metals. The composition of cellulose, hemicellulose and lignin can vary from one wood species to another, as can be seen in Table 4.1.

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Table 4.1 Cellulose, Hemicellulose, and Lignin Content in Pine, Birch, Poplar and Beech wood.

Biomass	Cellulose [%]	Hemicellulose [%]	Lignin [%]	Impurities [%]
Pine	51	23	22	5
Birch	45	28	22	5
Poplar	52	23	21	4
Beech	47	23	22	8

Four type of wood such as: pine, birch, poplar and beech were selected.

By analysing Table 4.1, it was possible to observe differences between amount of cellulose, hemicellulose lignin in different wood samples. It was also possible to identify smaller amount of impurities which can consist of soluble non- structural materials such as non-structural sugars, nitrogenous material, chlorophyll, and waxes, as reported in the literature [19]. The difference in the structure and chemical composition between the lignocelluloses affects their affinity for depolymerisation and consequently the yield of the products that can be obtained.

The highest amount of cellulose (52%) was observed in the case of poplar, followed by pine wood (51%), beech (47%) and finally birch wood (45%).

There is a significant variation of the cellulose content of the wood samples, which depend on whether it is derived from hardwood or softwood.

Poplar is an example of hardwood. Generally, hardwoods have more complex structures than softwoods containing large water conducting pores or vessels that are surrounded by narrower fibre cells [22]. Beech is also included in hardwood group, however contains lower amount of cellulose than poplar.

On the other hand, pine belongs to softwood which is very abundant, because softwoods are among the most important commercial trees grown in large plantations. It is also the most recalcitrant feedstock type. In general, softwoods contain higher amount of lignin as can be seen in obtained results. It is considered to be the reason for its higher resistance to delignification compared to grass or hardwood biomass [22]. Birch is also considered as softwood, however showed lower amount of cellulose and higher hemicellulose than pine.

It is important to mention that the percentages of the three components can also be influenced by harvesting time and how they were cultivated.

4.1.1.2 Characterization of the properties of different biomass samples by powder X-ray diffraction (XRD) technique

In order to better understand the relationship between cellulose structure and their properties, one of the aim of this work was to understand the main structural differences between investigated woods. For this reason, X-ray diffraction (XRD) was applied.

X-ray diffractograms collected from pure cellulose and pure wood are shown in Figure 4.1.

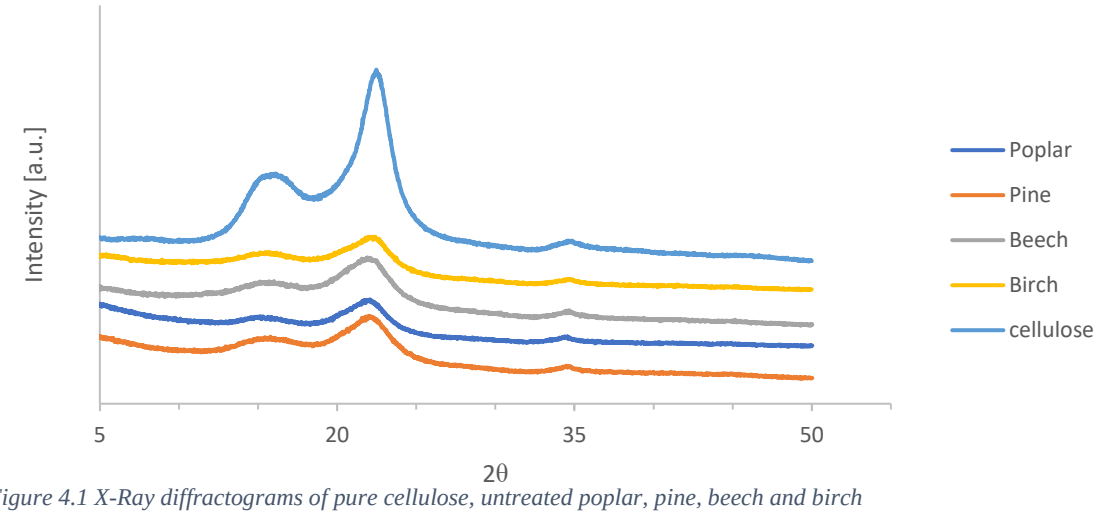

Figure 4.1 X-Ray diffractograms of pure cellulose, untreated poplar, pine, beech and birch

XRD gives the information of the atomic arrangement within the structural building block (called "unit cell") that repeats infinitely along all three Cartesian coordinate directions. The diffraction peak measured at a specific angle (θ) corresponds to a spacing between atomic planes reflecting x-ray. Thus, 2θ is the incidence and reflection angle [57].

The diffraction curves correspond to the contribution of the crystallographic and amorphous phase.

To better understand the diffractograms of the investigated samples, the crystallographic planes were identified according to the pure cellulose structure described in JCPDS data base (ref:00-003-0289), as can be seen in Appendix A. The pure cellulose corresponds to cellulose I,

which is the crystalline cellulose that occurs in the nature compositing of two distinct crystalline modifications, namely Iα and Iβ, whose fractions vary depending on the origin of the cellulose sample [58].

By analyzing the diffractogram of pure cellulose it is possible to conclude that main peak at 22.75º 2θ is assigned to crystallographic plane (002) and signal of 2 theta equal 15.97º origins from overlapping of the two signals at 14.90º and 16.49º 2θ which corresponds to the the crystallographic planes (101) and (10i) respectively. Similar results can be also found in the literature [59]. In case of the peak with lower intensity at 34.9º 2θ corresponds to crystallographic plane (040).

The XRD measurements demonstrated that in the pure cellulose the three major reflexes were identified sample at 15.97º, 22.75º and 34.92º 2θ.

By comparing the XRD spectra of different wood samples it was possible to observe differences in intensity of peaks. It was also noted that all wood sample revealed the same crystallographic structure in comparison with X-ray diffraction curve of pure cellulose.

Independently of the sample, three major signals at the values of 2 theta equal 15.89º, 22.18º, 34.65º 2θ were observed, which correspond to the crystallographic plane as described above. On the other hand, the more pronounced difference occurs at the main peak reflection at 22.18 2θ, which is assigned a crystallographic plane of cellulose (002).

It should be mentioned that the woods contain lignin and hemicelluloses as well, which are amorphous in nature and their diffraction peaks are rather broad and difficult to analyse.

Additionality, the intensity of the signals corresponding to amorphous and crystallographic phase was used to calculate the crystallinity index.

It was determined for the various samples and the results are summarized in Table 4.2.

Crystallinity index was calculated based on the formula proposed by Segal *et al*.

$$CI = [(I_{(002)} - I_{am})/I_{(002)}] \times 100\ \%$$

where: $I_{(002)}$- intensity of the crystalline signal of cellulose (002) I_{am}- intensity of the amorphous signal.

Table 4.2 Crystallinity index of pure cellulose and different type of pure wood determined by XRD method

Biomass sample	CI [%]
Cellulose	70
Poplar	79
Pine	68
Beech	65
Birch	66

According to the calculations, all tested wood samples have similar crystallinity index (CI) in the range of (66-70).

Similar values of CI were observed for pine, beech and birch with 68%,65% and 66% respectively.

The obtained results exhibited also that the highest value of crystallinity index corresponded to poplar wood. This could be due to the fact that on that sample the amount of cellulose was higher in comparison to other wood samples, as can be seen in the Table 4.1. In the case of pine, beech and birch, when it takes into account of the amount of cellulose, this is in accordance with crystallinity index results as well.

On the other hand, when it comes to the CI of pure cellulose, surprisingly presented lower value (70%) than poplar.

It should be mentioned that the crystallinity index value can be influenced for several factors. One of them is relate do the source of feedstock e.g. how old it is, and how the wood was cultivated, what was the initial pre-treatment and storage conditions. Other important aspect, which must be mentioned is that the crystallinity degree can have an important role in hydrolysis of cellulose.

4.1.1.3 Fourier transform infrared spectroscopy (FTIR) used for characterization of the biomass surface

All the obtained samples were analysed by FTIR spectroscopy. This technique permits to realise a qualitative and quantitative analysis. However, note that for quantitative analysis, this technique is not rigorous and the results obtained are seen as estimated values.

FTIR spectroscopy has been used often in many studies of biomass materials [59]- [61]. Very often in those studies KBr was used for pellets preparation. Therefore, in the first step of our work we investigated the influence of the KBr.

It was found that the presence of KBr in the pellet can be a problem during FTIR analysis, specially, in the finger print region within the 1800-650 cm^{-1} range.

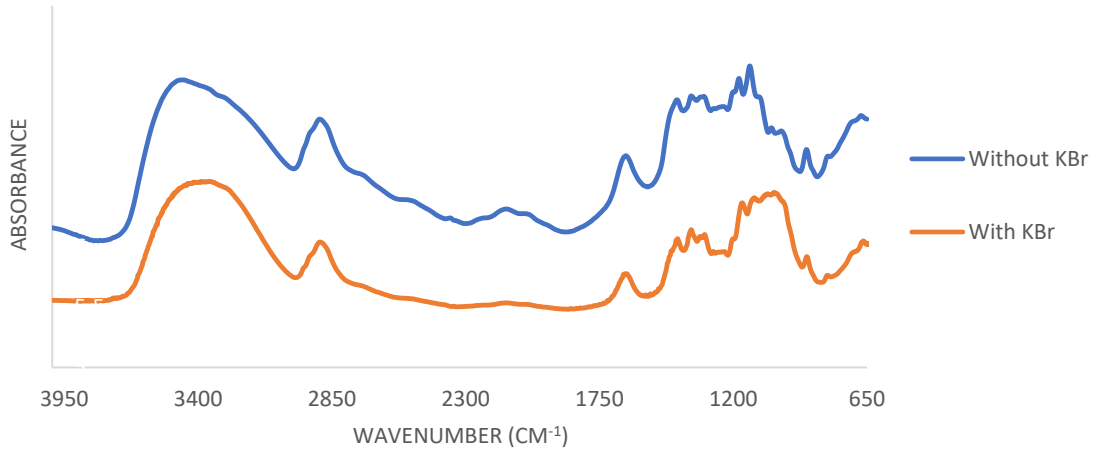

Figure 4.2 Infrared spectra of pure cellulose with and without KBr.

The Figure 4.2 shows infrared spectra of pure cellulose with and without KBr addition.

It was possible to observe differences in the fingerprint region in the spectra of the both samples.

Several shifted bands were observed in the case of measurement with KBr such as: 1177 cm^{-1} to 1163 cm^{-1}, 1131 cm^{-1} to 1113 cm^{-1}, 1086 cm^{-1} to 1063 cm^{-1} and 1032 cm^{-1} to 1027 cm^{-1}. This indicates that KBr can "interact" with biomass samples and change some position of bands.

Then, for further analysis, the FTIR measurements without KBr were chosen. The results for FTIR analysis with biomass samples are presented in Figure 4.3.

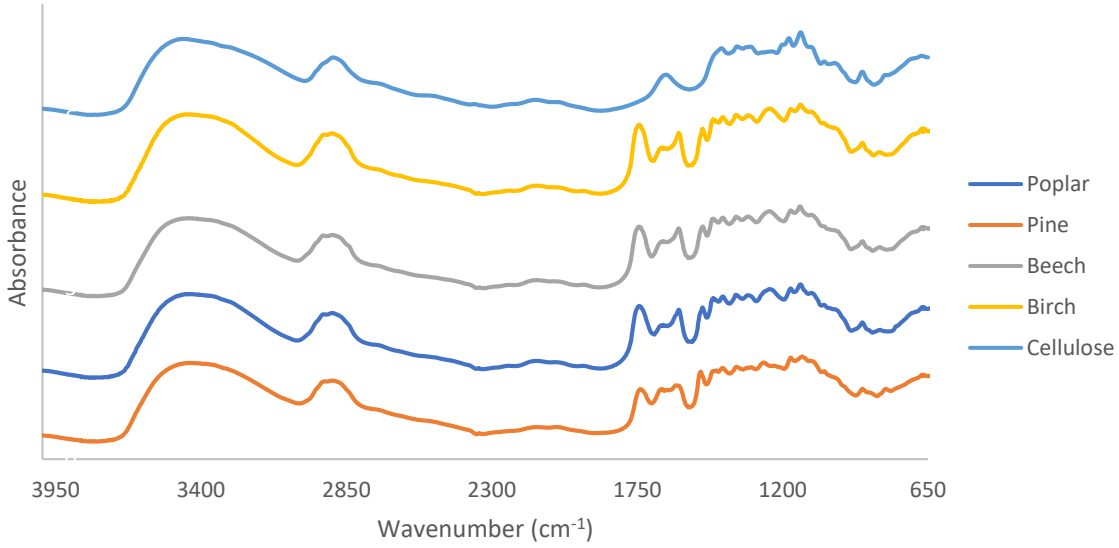

Figure 4.3 Infrared spectra of pure cellulose and different type of pure wood such as poplar, pine, beech and birch.

According to the infrared spectra of cellulose, several bands were identified. The typical functional groups and related wavenumbers were placed in the Table 4.3 as reference.

The table revels that for investigated samples we can identify the following groups alkene, esters, aromatics, ketone and alcohol, with different oxygen-containing functional groups, e.g., OH (3400–3200 cm^{-1}), C=O (1765–1715 cm^{-1}), C–O–C (1270 cm^{-1}), and C–O–H (~1050 cm^{-1}) [62].

Table 4.3 FTIR frequency range and functional typical functional group present in lignocellulose [62].

Wavenumber (cm^{-1})[a]	Functional groups	Possible Compounds
3600–3000 (s)	OH stretching	Acid, methanol,Water
2860–2970 (m), 1700–1730 (m),	$C–H_n$ stretching	Alkyl, aliphatic, aromatic
1510–1560 (m)	C=O stretching	Ketone and carbonyl
1632 (m)	C=C	Benzene stretching ring
1613 (w) 1450 (w)	C=C stretching	Aromatic skeletal mode
1470–1430 (s)	$O–CH_3$	Methoxyl–O–CH3
1440–1400 (s)	OH bending	Acid
1402 (m)	CH bending	
1232 (s)	C-O-C stretching	Aryl-alkyl ether linkage
1215 (s)	C–O stretching	Phenol
1170 (s), 1082 (s)	C–O–C stretching vibration	Pyranose ring skeletal
1108 (m)	OH association	C–OH
1060 (w)	C–O stretching and C–O Deformation	C–OH (ethanol
700–900 (m)	C–H	Aromatic hydrogen
700–400 (w)	C–C stretching	

[a] s: strong, m: middle, w: weak

In the case of the spectra of woods, similar bands to the spectra of cellulose were observed. However, it was also possible to observe more bands, which origin from different functional groups present in lignin and hemicellulose.

The literature reports that the highest IR absorbance of OH and C–O was found with cellulose while hemicellulose contained higher number of C=O groups. By comparison with hemicellulose and cellulose, a big difference was identified in the finger print region at 1830–730 cm^{-1} range for lignin's IR spectra. A group of complex IR absorbance of lignin was found there, indicating that lignin might be rich of methoxyl–O–CH_3, C–O–C and C=C (aromatic ring) containing compounds due to the presence of C=C and C–O–C vibrations [60] [62].

Analysing each spectra, (Figure 4.3), it can be seen that several bands appears in woods spectra which are not present in cellulose spectra.

Band of the strong intensity at 1743 cm^{-1} is visible in all wood samples spectra and almost not visible in cellulose. This vibration which is not observed in the cellulose spectrum is characteristic of the presence of C=O functional group. The bands present at 1249 cm^{-1},1501 cm^{-1} and 1592 cm^{-1}, are also invisible in cellulose infrared spectra. They are related with the C-O-C stretching (associated to aryl-alkyl ether linkage), C=O stretching vibrations (assigned to ketone and carbonyls), and C=C stretching (associated to aromatic skeletal mode) respectively.

4.1.1.4 Characterization of the morphology of biomass sample by Scanning electron microscopy (SEM)

The last part of the characterization of biomass samples was devoted to the scanning electron microscopy (SEM) measurements. It was performed to all samples (pure cellulose and pure woods). The results are shown in Figures 4.4, 4.5, 4.6 and 4.7.

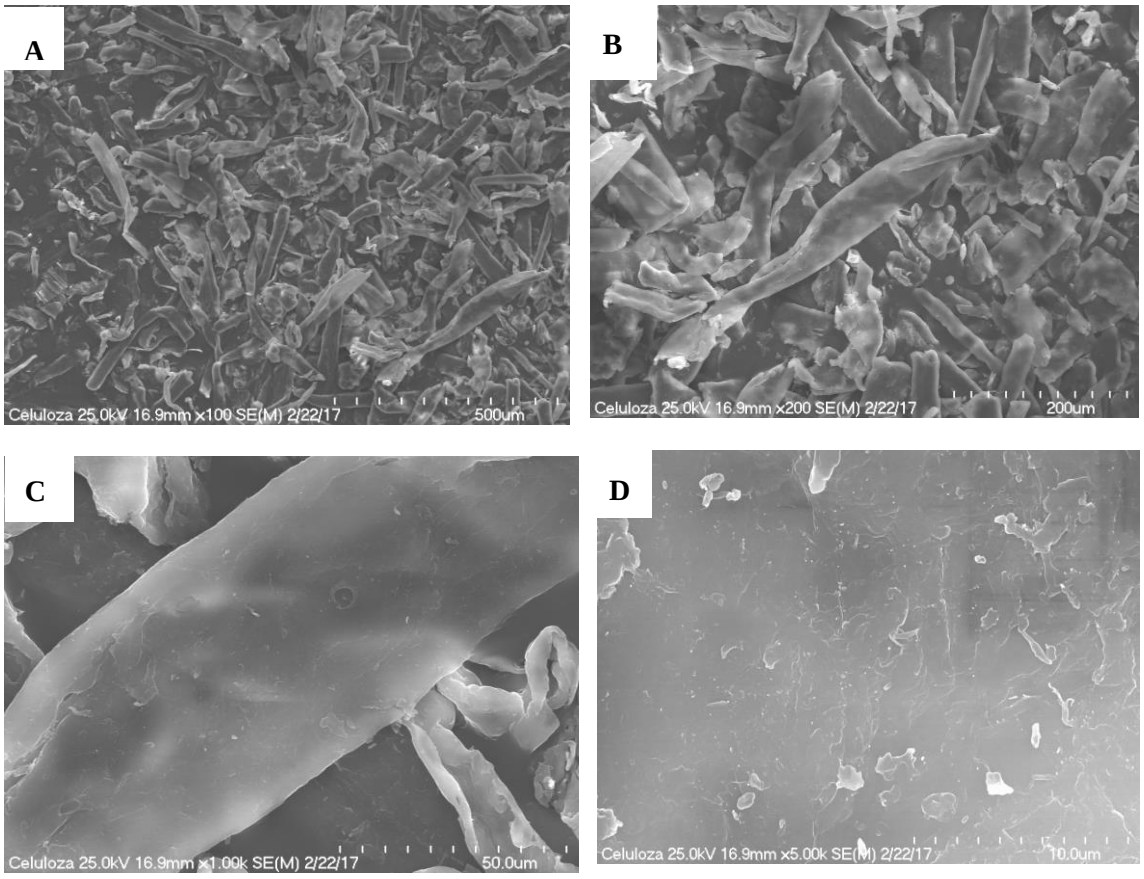

Figure 4.4 SEM images of pure cellulose (A and B- lower magnification, C and D -higher magnification).

The Figure 4.4 demonstrates images of pure cellulose under various magnifications.

The Figs. 4.4A and 4.4B clearly show the shapes and size distributions of the fibers of the investigated sample. It is possible to observe that the fibers are well separeted and their diameters are almost the same. It is also possible to note that the strutures of fibers are regular and uniform.

In the case of the SEM images (Fig. 4.4C and 4.4D) of one individual exemplay fiber at larger magnification show that the surface of untreated sample is smooth and almost free of demages.

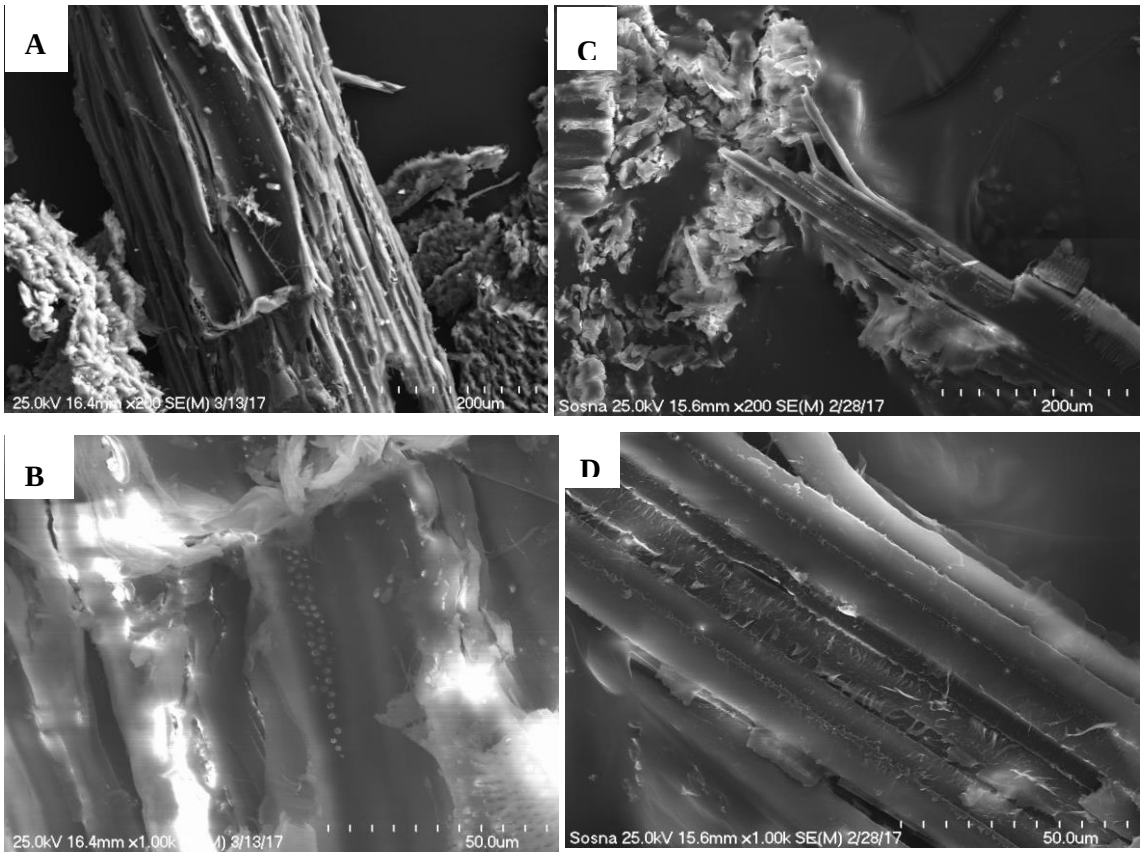

Figure 4.5 SEM images of pure wood (A and B Birch images with lower and higher magnification respectively) (C and D Pine images with lower and higher magnification respectively).

In the next step the characterization of wood was also performed by SEM.

The results for birch and pine sample are presented in Fig 4.5 under lower (A and C images) and higher (B and D images) magnification.

Both samples showed a clear structure containing fibers, which promotes a compact form.

A closer look at the fiber surface (Fig. 4.5 B and D) at larger magnification show that some holes and damage are present.

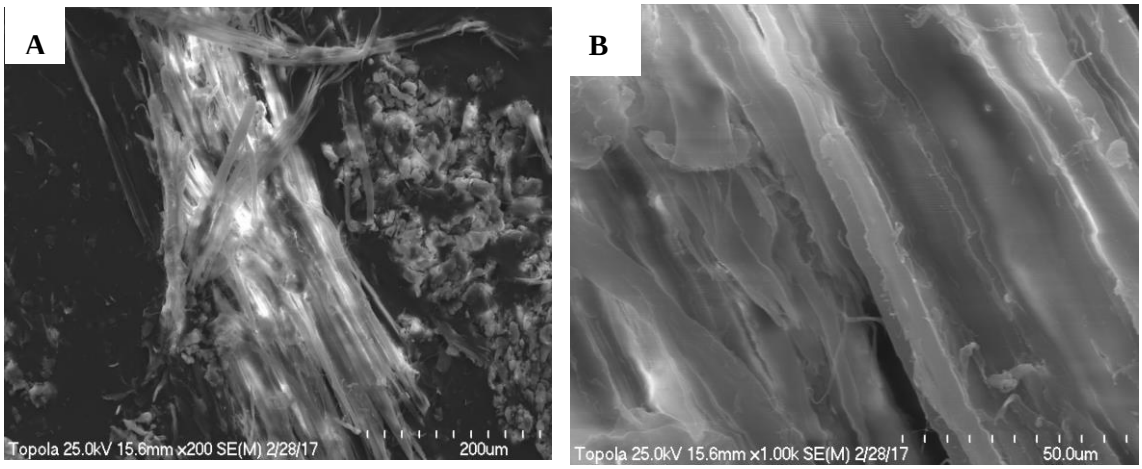

Figure 4.6 SEM images of Poplar at low (A) and high(B) magnification.

In the case of poplar (Fig.4.6), it was also possible to observe a fibrous structure. At high magnification of one individual fiber (image B), it can be noticed that there are some damages present, also the structure is not so uniform like in the case of cellulose

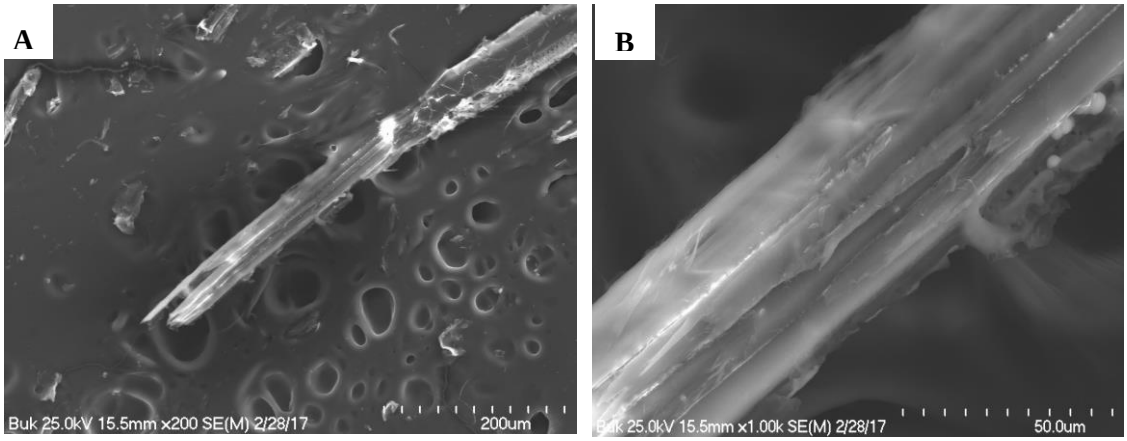

Figure 4.7 SEM images of Beech at low (A) and high (B) magnification.

On the other hand, when it comes to the images of beech wood, lesser fibers was observed. Visible holes and irregular form of one individual fiber (image B) was also noted.

4.2 Hydrolysis of cellulose

In order to evaluate the hydrolysis of cellulose of the different biomasses, the acid hydrolysis of these samples was performed. The hydrolysis was carried out with 0.9%wt of H_2SO_4 and the results are presented in Table 4.4.

Table 4.4 Obtained results after acid hydrolysis of biomass samples with the use of 0.9% H_2SO_4.

Biomass	Conversion [%]	LA yield [%] *	FA yield [%] *
Pine	87	50	32
Birch	94	31	31
Poplar	92	38	26
Beech	97	41	39
Cellulose	87	50	44

*Based on cellulose content

After hydrolysis of cellulose, levulinic acid (LA) and formic acid (FA) were identified as major components. According to the results of biomass composition, different amount of LA and FA in all wood samples were observed.

The highest yield of LA was observed for cellulose (50%) and for pine tree, the lowest value was found for birch wood in this case only 31 % of LA yield was observed.

The formic acid is formed in equimolar amount with the levulinic acid in the reaction, so theoretically the same amount of those two molecules should be observed. This was however not the case in all reactions as the differences in their yield were noticed.

Only for two cases when hydrolysis was performed with birch and beech wood the same (31%-31%) and almost the same (41%-39%) yield of LA and FA respectively was observed.

It was also possible to observe differences between conversions in all studied samples.

Birch and beech presented higher crystallinity index and the highest conversion, (94% and 97% respectively) as well. Cellulose crystallinity is considered to be an important factor to evaluate the accessibility of cellulose to be hydrolysed. As can be seen, the tree with high CI high also presented high conversion.

Surprisingly, the opposite situation was noted in the case of pine and poplar. In the case of pine, 18% of difference between LA and FA were observed. In addition, 12% of difference was identified in the case of poplar. Also for reaction with cellulose there was visible difference, the yield of LA was 50% whereas for FA only 44%.

Other explanation can be related with the occurrence of the decomposition of the FA. This is however not the only factor, as those values can depend as well on the side reactions, the presence of the impurities and finally the composition of the biomass.

4.3 Influence of the pH in levulinic hydrogenation and formic acid decomposition

The synthesis of GVL directly from biomass is a real challenge. This reaction needs to be done in the two steps (acidic hydrolysis of cellulose followed by hydrogenation). During the biomass hydrolysis, many other products are formed that can also undergo hydrogenation. Moreover, the lignin and hemicellulose contain many other impurities that are harmful to metal active sites. Therefore, hydrogenation of levulinic acid to GVL is a difficult process.

For this reason, in this work, the influence of several parameters for biomass hydrolysis on the subsequent LA hydrogenation towards GVL were studied.

The hydrolysis of biomass was conducted in the presence of sulphuric acid. Therefore, the first parameter which was analysed was the effect of the pH of the reaction mixture on the activity of the catalysts in the subsequent reactions. In order to better understand this effect during formic acid decomposition and subsequent levulinic acid hydrogenation, two separate reactions were performed.

The reactions were performed in two conditions: one using 0.9% sulphuric acid as solvent and other with pure water was carried out for a comparison. They were performed during 5h with the same catalyst 5%Ru/C. The results are shown in Table 4.5.

Table 4.5 Effect of sulphuric acid in the simultaneous FA decomposition and hydrogen transfer reaction to LA hydrogenation.

Catalyst	Solvent	FA conversion [%]	LA conversion [%]	GVL Yield [%]
5% Ru/C	0.9%wt H_2SO_4	90	21	8
	water	100	61	45

[a] Reaction condition: 190ºC;5h; 26 ml of 0.9%H_2SO_4 /water as a solvent; 0.122 ml of FA,0.36g of LA and 0.2g of catalyst

The hydrogenation of levulinic acid was performed with formic acid as a hydrogen source. According to the Table, reaction in the simultaneous formic acid (FA) decomposition and levulinic acid (LA) hydrogenation performed in water revealed higher catalytic performance than in the presence of sulphuric acid. In the latter case, full conversion of FA and 61% of LA conversion were obtained. In addition, 45% of GVL was formed.

On the other hand, in the presence of sulphuric acid, low conversion of levulinic acid and consequent small amount of GVL were observed. Several factors can be responsible for these results. First, the presence of sulphur containing species can poison the metal catalyst that is the active site for the hydrogenation reaction. The other reason can be related to the pH, which becomes too low in the presence of sulphuric acid which can influence negatively the reaction.

In general, the process consists of two steps: formic acid decomposition and levulinic acid hydrogenation. Then, it was important to understand which step is more influenced by the pH.

For this reason, FA decomposition and LA hydrogenation were performed independently with the same catalyst and pH was measured after reaction. The results are shown in Table 4.6.

Table 4.6 Effect of sulfuric acid in individual reactions: LA hydrogenation with external hydrogen source and FA decomposition.

Solvent	pH	LA hydrogenation [a]		FA decomposition [b]				
		GVL Yield [%]	LA conversion [%]	FA conversion [%]	Gaseous product amount [vol%]			
					H_2	CH_4	CO_2	CO
0.9% H_2SO_4	1	78	98	68	16	2	58	25
H_2O	3	70	98	85	25	4	56	15

[a] Reaction condition: 0.2g of 5Ru/C catalyst; 190ºC, 1h, 26 ml of solvent, external source of hydrogen (15 bar). [b] Reaction conditions: 190ºC; 1h; 122 ml of FA; 26 ml of solvent and autogenic pressure.

In general, no matter whether the reaction was carried out with sulphuric acid or water, ruthenium catalysts showed high performance in the hydrogenation of levulinic acid towards GVL.

Fully different behaviour was observed for FA decomposition. The lowest conversion (68%) in the decomposition of formic acid was noted when the reaction was performed at lower pH in comparison with reaction in water.

Formic acid decomposition is a crucial step for the production of GVL because during dehydrogenation, formic acid also decomposes into hydrogen which is used as an internal hydrogen source in the LA hydrogenation into GVL. As can be seen higher yield (%) of hydrogen was produced in pure water used as the reaction solvent in contrast to reaction done in the presence of sulphuric acid. This suggests that in the presence of low pH, decomposition of FA into hydrogen and CO_2 becomes difficult due to inhibition of the formic acid dissociation towards formate. Formic acid can also decompose via dehydration path in the case of CO and H_2O are formed. It was also possible to observe the formation of CH_4, which results from the secondary reactions, which is also observed in the literature [34].

In order to have the more detailed information the influence of the basic pH was also checked. Levulinic acid hydrogenation and formic acid decomposition were performed in the high pH, with the use of 0.7%sodium hydroxide. The reactions were performed under the same conditions as above. The results are shown in Table 4.7.

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Table 4.7 Effect of sodium hydroxide in individual reactions: LA hydrogenation with external hydrogen and FA decomposition.

Solvent	pH	LA hydrogenation [a]		FA decomposition [b]				
		GVL Yield [%]	LA conversion [%]	FA conversion [%]	Gaseous product [vol%]			
					H_2	CH_4	CO_2	CO
0.7% NaOH	11	74	100	90	29	4	58	12
H_2O	3	70	98	85	25	4	56	15

[a] Reaction condition: 0.2g of 5%Ru/C catalyst; 190ºC, 1h, 26 ml of solvent, external source of hydrogen (15 bar). [b] Reaction conditions: 190ºC; 1h; 122 ml of FA; 26 ml of solvent and autogenic pressure.

Contrary to acid environment, in basic pH a high conversion of LA and FA were obtained, which makes evident that the pH has influence on the reactions, especially during formic acid decomposition.

The literature reports state that the formic acid is excellent hydrogen donor. The presence of sodium hydroxide in the solution facilitates the dissociation of FA to sodium formate which is the first step in the formic acid decomposition. The presence of formate anion significantly accelerates the hydrogen generation rate, meaning that the aqueous solution of formate is decomposing much more easily thus promoting the dehydrogenation. Analogous behaviour was also reported in the literature [63]. This could explain why the conversion of formic acid is higher in that case than in lower pH, because, the presence of acid environment does not provide the occurrence of formate as easily as in the basic environment.

In general, the results showed big influence of pH in the reaction, especially during the formic acid decomposition. In the case of high pH almost full conversion was obtained of formic acid in comparison to reaction conducted in low pH (68% of FA conversion).

As the strong influence of basic pH was found, the addition of alkaline compound was studied in the next step.

4.4 Influence of the addition of the alkaline compound

As mentioned, pH has a great influence on the efficiency of the catalyst activity, especially during decomposition of formic acid. One of the solutions to increase the pH is by addition of alkaline compound.

For this reason, the reaction with LA hydrogenation and formic acid decomposition in the presence of sulphuric acid as solvent was performed with addition of different alkalines. The reactions were carried out under the same conditions in the same stoichiometric amount between solvent (sulphuric acid) and alkaline compound. Then, the following alkaline compounds were selected NaOH, CaO, $Ca(NO_3)_2$ and $CaCO_3$.

In the table 4.8 shows the results of the investigated reactions are presented.

Table 4.8 The influence of different alkaline compound acid in the simultaneous FA decomposition and hydrogen transfer reaction to LA hydrogenation [a].

Catalyst	Alkaline compound	pH	FA conversion [%]	LA conversion [%]	GVL Yield [%]
5%Ru/C	NaOH	5	100	53	41
	CaO	3	78	36	17
	$Ca(NO_3)_2$	3	100	49	0
	$CaCO_3$	4	100	50	32

[a] reaction condition, 26ml of 0.9% H_2SO_4,0.36g of LA,0.122ml of FA, stoichiometric amount of alkaline compound (0.192g of NaOH, 0.244g of $CaCO_3$,0.13g of CaO and 0.56g of $Ca(NO_3)_2$), 5h, 190ºC $pH_{initial}$ =1

Depending on the type of alkaline compound the effect on the solution was different.

Sodium hydroxide is a very common and strong base used in the chemical industry. It was observed that after its addition, the pH increased from 1 to 5 and full conversion of formic acid was obtained. Additionally, 54% of LA conversion and 41% of GVL yield were presented. It is important to notice that sodium hydroxide reacted with formic acid towards sodium formate which facilitated the dissociation and the subsequent reaction.

In the case of CaO, $Ca(NO_3)_2$ and $CaCO_3$ the contact with H_2SO_4 created a precipitate, which can be removed from the reaction. However, calcium has a strong interaction with levulinic acid and formic acid creating salts too.

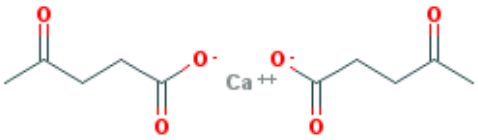

Figure 4.9 Illustration of calcium levulinate [73].

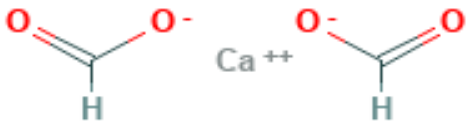

Figure 4.8 Illustration of calcium formate [74].

The illustrations of the salts structures are shown in the following figures.

The formation of these two salts represent a problem for this process, because during the separation of sulphate from the solution, levulinate and formate are removed as well. As a consequence, the reaction solution will contain lower amount of substrate, which are used to produce GVL.

In the case of $Ca(NO_3)_2$ which dissociates easily and as a consequence the formation of levulinate and formate create immediately. The precipitate formed was removed from the solution together with calcium sulphate. In the case of CaO the mechanism is different as it is a solid so also the reaction with H_2SO_4 occurs slowly to some extent only, however as it can also leach to the solution the formation of the formate and levulinate can also occur. This can explain why LA conversion and GVL yield in the both case was such low.

The reaction with $CaCO_3$, high yield of GVL was obtained. $CaCO_3$ in presence of sulphuric acid creates sulphate carbonate. In fact, $CaCO_3$ creates a precipitate with LA and FA as well. However, according to the LA and FA conversion, it seems that the interactions are not as strong as in the case of the $Ca(NO_3)_2$ and CaO.

The highest yield of GVL was obtained by addition of NaOH. Therefore, this adduct was chosen for further tests. In the next step, the influence of the NaOH concentration was investigated. The ratio of sodium hydroxide to the H_2SO_4 was varied starting from stoichiometric amount (1:1), then double excess (1:2) and in (1:0.75) of the stoichiometric amount.

Table 4.9 . Influence of the amount of NaOH in the simultaneous FA decomposition and hydrogen transfer reaction to LA hydrogenation on the Ru/C catalyst [a].

Catalyst	Amount of NaOH(g)	pH	FA conversion [%]	LA conversion [%]	GVL Yield [%]
5%Ru/C	0.384 (1:2)	10	100	38	37
	0.192 (1:1)	5	100	53	41
	0.144 (1:0.75)	4	94	35	25

[a] reaction condition, 26ml of 0.9% H_2SO_4,0.36g of LA,0.122ml of FA, 5h, 190ºC $pH_{initial}$ =1

According to the Table 4.9, the lower amount of NaOH is accompanied by the decrease of GVL yield. It is important to notice that in that case only 94% FA and 35% LA conversion were observed, which means that probably 0.75 of amount of NaOH is not enough for the process.

On the other hand, when the amount of NaOH was increased to double, full conversion of FA was obtained, however, 38 % LA conversion and 37% GVL yield were formed. Double amount of this base increased the pH from 1(before the reaction) to 10 (after the process), making the environment completely basic. This suggests that, when the solution contains a lot of OH group the transfer of hydrogen to levulinic acid hydrogenation becomes difficult.

The presence of H_2SO_4 creates the acidic environment which has negative influence on the reaction additionally it can poison the catalytic surface. Therefore, in order to neutralize the mineral acid and remove it from the hydrolytic mixture and additionally to create the basic environment which is beneficial for the FA decomposition the dual approach was undertaken.

The reaction was performed in the presence of $CaCO_3$ and NaOH together in FA decomposition and subsequent LA hydrogenation reaction. The results are shown in Table 4.10.

Table 4.10 Simultaneous formic acid decomposition with levulinic acid reaction by addition of $CaCO_3$ and NaOH.

Conditions test	Catalyst	pH	FA conversion [%]	LA conversion [%]	GVL Yield [%]
Acid hydrolysis 0.9%wt H_2SO_4, stoichiometric amount of $CaCO_3$ (0.24g), stoichiometric amount of NaOH (0.192g)	5%Ru/C	10	94	28	17
Acid hydrolysis 0.9%wt H_2SO_4,, stoichiometric amount of $CaCO_3$ (0.24g), half stoichiometric amount of NaOH (0.048g)		5	100	50	26

The two reactions were performed with different amount of $CaCO_3$ and NaOH.

First, reaction was performed with the stoichiometric amount of both compounds to sulphuric acid and second with stoichiometric amount of $CaCO_3$ and half stoichiometric amount of NaOH. In general, both reactions the amount was calculated taking into account the amount of sulphuric acid.

The use of calcium carbonate allowed to remove sulphate from the solution, however low pH was still observed. Then, the addition of NaOH provided the increase of the pH.

In the case of the reaction performed with the half amount of NaOH, 50% of LA conversion and 26% GVL was obtained with pH increasing to 5.

On the other hand, when the same stoichiometric amount of $CaCO_3$ and NaOH to sulphuric acid high pH (pH=10) was observed. However, low GVL yield was obtained and LA conversion as well. This is in accordance with previous result, confirming that high pH probably makes difficult the transfer of H_2 to levulinic acid.

The achieved results permit to conclude that, the addition of NaOH seems to be a good solution to increase the pH. However, increase or decrease more than stochiometric amount of

sodium hydroxide did not show high reaction performance even with addition of calcium carbonate. Therefore, for the following it was decided to focus the reaction on the formic acid decomposition with levulinic acid hydrogenation with the use of sulfuric acid as a solvent and addition of sodium hydroxide in stoichiometric amount.

4.5 Influence of the reaction conditions

In the next step of the investigations, two other parameters were analysed on the reaction conditions namely: influence of the type of the catalyst and reactor were checked. Then, to better understand several reactions were performed.

4.5.1 Influence of the catalyst

Ruthenium supported on carbon catalyst was chosen because this catalyst has demonstrated a good performance in hydrogenation of LA towards GVL with formic acid (FA) as a hydrogen source [34] [64]. However, in the reaction with real biomass feedstock it represents a challenge. Therefore, in order to analyse the activity of the catalyst of Ru/C in comparison with other catalyst 4% Ni-Au/Al_2O_3 and 5%Ru/10%Ca-TiO_2 were selected.

Table 4.11 presents the results obtained from the chosen catalysts. The reactions were carried out under same conditions.

Table 4.11 Activity of selected catalyst in the simultaneous FA decomposition and hydrogen transfer reaction to LA hydrogenation. [a]

Catalyst	FA conversion [%]	LA conversion [%]	GVL Yield [%]
5%Ru/C	100	53	41
4% Ni-Au/Al_2O_3	90	13	13
5%Ru/10%Ca-TiO_2	97	1	0

[a] Reaction condition: 190ºC; 5h; 26 ml of 0.9%H_2SO_4 as a solvent;0.192g of NaOH (1:1), 0.122 ml of FA;0.36g of LA and 0.2g of the catalyst.

It is possible to observe that the highest (41%) GVL yield was obtained with 5%Ru/C, followed by 4% Ni-Au/Al_2O_3 (13%) and 5%Ru/10%Ca-TiO_2 (0%).

On the other hand, modification of the titania support to obtain basic properties by addition of calcium showed higher activity in formic acid decomposition. However, 5%Ru/10%Ca-TiO_2 catalyst did not show any activity in hydrogenation of LA with formic acid (FA) as a hydrogen source in presence of sulphuric acid, as can be seen in Table 4.11.

In the case of Au-Ni system low activity was observed in this reaction as well, which was surprising, because this catalyst has demonstrated a great performance in the simultaneous formic acid decomposition and levulinic acid hydrogenation reaction in water. Those differences will be explained later in the chapter related to catalysts characterization.

In spite of Ru/C catalyst presented the highest activity, difference between (53%) LA conversion and (41%) GVL yield was observed. Any other products were not identified in this reaction. This difference can be explained by several factors. The adsorption of the levulinic and GVL on the carbon surface can be the first reason, which was proved by Ruppert et al [34]. that carbon can adsorb 15% of LA and 5% of GVL due to the high surface area of active carbon. The other can be related to the decomposition of the product.

4.5.2 Influence of the reactor

Table 4.12 Influence of the reactor in the simultaneous FA decomposition and hydrogen transfer reaction to LA hydrogenation

Berghof reactor			**Parr reactor**		
FA conversion [%]	**LA conversion [%]**	**GVL Yield [%]**	**FA conversion [%]**	**LA conversion [%]**	**GVL Yield [%]**
100[a]	71[a]	53[a]	100[a]	53[a]	41[a]
100[b]	67[b]	52[b]	100[b]	41[b]	32[b]

[a] Reaction condition: 190ºC, 5h, 26 ml of 0.9%H_2SO_4 as a solvent, 0.192g of NaOH, 0.122 ml of FA,0.36g of LA and 0.2g Ru/C catalyst. [b] Reaction condition: 190ºC, 5h, 26 ml of 0.9%H_2SO_4 as a solvent, 0.244g of $CaCO_3$, 0.122 ml of FA,0.36g of LA and 0.2g Ru/C catalyst

The next parameter studied was the influence of the reactor. Berghof reactor was selected, which contains smaller volume than previous one (Parr reactor). The reaction was performed in two ways: adding NaOH or $CaCO_3$.

The reaction with addition of $CaCO_3$ was chosen for comparison, as promising results were observed in the case of this adduct as well. The results are presented in Table 4.12.

The same catalytic performance in reaction with presence of NaOH and $CaCO_3$ was observed. In the case of addition of NaOH, 71% of LA conversion and 53% of GVL yield were obtained. In respect to $CaCO_3$, 67% of LA conversion and 52% of GVL yield were noted. Full conversion of formic acid was presented in both reactions.

However much better results were obtained in the reactor of smaller size that contains the smaller volume of reaction mixture. That can be related to the volume of the reactor, which provides better contact between the catalysts surface and substrate and reagent, in comparison with Parr reactor. For this reason, FA decomposition and LA hydrogenation can run much easier.

4.6 Direct hydrolytic hydrogenation

After choosing all parameters, (addition of NaOH, 5%Ru/C as catalyst and Parr reactor), it was possible to verify the catalyst activity in the conversion of pure cellulose and pure wood toward GVL. The reaction was performed into two steps, the first was hydrolysis of biomass and further hydrogenation of formed hydrolysis products. Reaction without addition of both alkaline compound was also performed for comparison (Table 4.13).

Table 4.13 Catalytic result for Ru/C in hydrogenation of formed hydrolysis products from cellulose without addition of NaOH and $CaCO_3$.

Catalyst	FA conversion [%]	LA conversion [%]	GVL Yield [%]
5% Ru/C	100	19	0

Firstly, it was conducted hydrogenation of formed hydrolysis products from cellulose without any change of conditions. In that case, full conversion of formic acid was observed. However, a very low conversion of LA was obtained with no GVL yield. On the other hand, as described in earlier chapter, formic acid decomposition is inhibited in low pH. Then, addition of

alkaline compound such as NaOH or $CaCO_3$ by increasing the pH can consequently improve this step. For this reason, hydrogenation of hydrolysis mixture from cellulose was performed with addition of NaOH as can be seen in the Figure 4.10. For comparison, the reaction with $CaCO_3$ addition was also conducted.

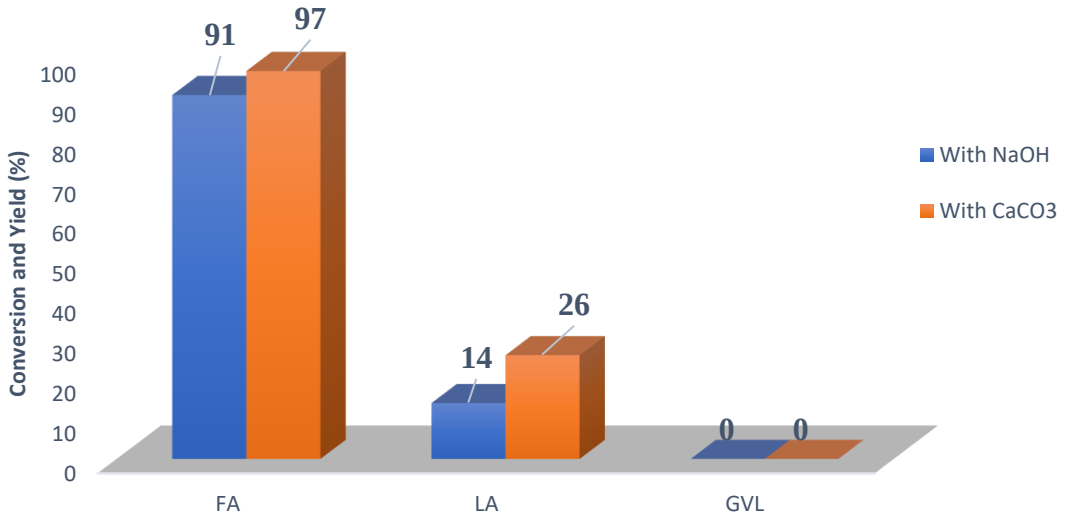

Figure 4.10 Catalytic result for Ru/C in hydrogenation of formed hydrolysis products from cellulose.

The hydrolytic hydrogenation of cellulose with addition of NaOH and $CACO_3$ presented low catalyst activity.

Ru/C showed high conversion of FA, 91% and 97% in the case of NaOH and $CaCO_3$, respectively, but with no production of GVL. In the case of LA conversion, low conversion was observed.

Based on the results from hydrolysis of different biomass samples (Table 4.4), the hydrolytic mixture obtained from birch wood was chosen because it showed same amount of levuninic acid and formic acid. This factor is very important, because the production of FA in equimolar amount to LA allows better biomass hydrogenation, since, FA is used as an internal hydrogen source in the LA hydrogenation into GVL [34]. The result is presented in Figure 4.11.

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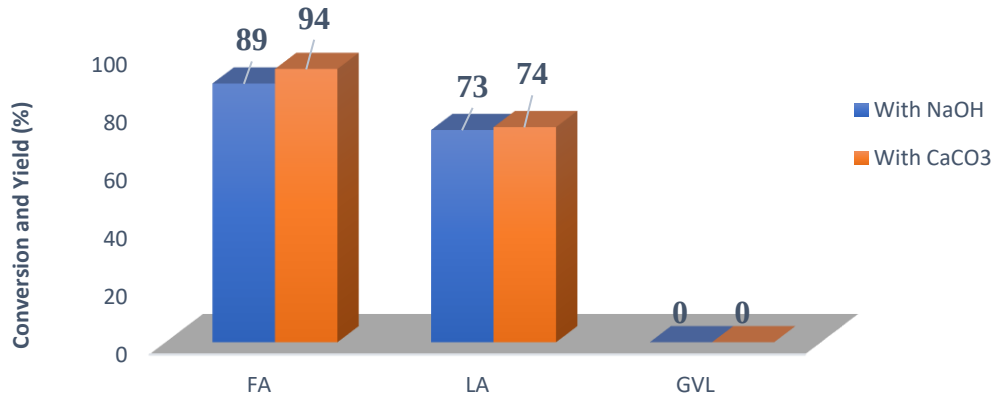

Figure 4.11 Catalytic result for Ru/C in hydrogenation of formed hydrolysis products from birch.

A similar effect was observed for the ruthenium catalyst used in hydrolytic hydrogenation of cellulose and in hydrolytic hydrogenation of birch. High conversion of formic acid with no production of GVL was also observed in the latter case. An example of such behaviour can be also found in the literature [35] [51]. However, from hydrolytic hydrogenation of birch, the highest LA conversion, 73% and 74% were observed in the presence of NaOH and $CaCO_3$ respectively (Figure 4.11).

It is important to note that conversion of biomass towards GVL is a great challenge due to several factors, such as the presence of impurities. Even, in the case of reaction with pure cellulose, humins in the reaction mixture are also formed in the first step (hydrolysis of cellulose towards LA).

The presence of impurities and humins can affect the reaction performance. The other reason can be the blocking of catalyst surface by reactants, carbon deposit formation or adsorption of impurities present in the reaction mixture.

On the other hand, differences between catalyst activity in reaction performed with pure cellulose and with birch wood was observed, especially in case of LA conversion. Then, a question arises why the hydrogenation of LA proceeds in some cases only to a small extent even after full decomposition of FA or proceeds without GVL production.

According to the literature, during the hydrogen transfer process, two reactions are competing: the dehydrogenation of formic acid and the hydrogenation of levulinic acid.

They can occur simultaneously or sequentially depending on the relative adsorption of the reactants. It was proved that formic acid adsorbs strongly and dissociatively on Ru in comparison with levulinic acid and occupies two Ru sites in this formate form [34].

For hydrogenation, it requires also the dissociative adsorption of H_2. However, due to strong adsorption of formic acid and consequence its dissociation in formate and then adsorption on Ru surface, the adsorption of LA and H_2 is blocked and the hydrogenation reaction is inhibited [34]. Catalyst can also be blocked by the strong adsorption on its surface the CO- by-product of the FA decomposition which inhibits its activity in the subsequent hydrogenation.

Answering the question, in the case of the hydrogenation products from hydrolysis of pure cellulose, LA conversion should be higher, because FA was fully decomposed and there was enough hydrogen available for subsequent step, additionally FA was not blocking active sites of catalyst.

In contrast, in the case of the hydrogenation mixture after birch hydrolysis, independently of which kind of alkaline compound was added, high conversion of FA and LA were observed. However, no GVL yield was identified, indicating that something happened during LA hydrogenation into GVL.

Moreover, it should be noted that pure wood contains more other compounds, which can derive from lignin and hemicellulose and, also more impurities than pure cellulose. Therefore, the reaction could proceed to other products, due to the multiple components present in the hydrolytic mixture is however difficult to deliberate the precise mechanism that could occur. The surface of the Ru catalyst could also be blocked by the carbon deposit or other impurities and sulphuric acid which could origin in changing the catalytic path of the reaction.

Summarizing several parameters, such as influence of pH, addition of alkaline compound, influence of catalyst and reactor were tested for synthesis of GVL directly from cellulose in hydrolytic hydrogenation without external hydrogen source. However, as it has been reported, valorisation of real biomass toward GVL is a great challenge, mainly because of many factors that can influence the reaction like impurities and other compounds presented.

In order to understand how strong is the effect of the impurities on the catalyst, those materials were characterized by two different methods.

4.7 Characterization of the catalyst

4.7.1 Time-of-flight secondary ion mass spectrometry (ToF-SIMS) analysis

In order to obtain information about the changes on the surface of the catalyst after reaction and to identify what kind of species are present on its surface time-of-flight secondary ion mass spectrometry (ToF- SIMS) was applied. This is a sensitive surface technique that allows to find not only elemental but also molecular information on the surface of the catalytic systems.

By applying this method, I wanted to understand the difference in the catalytic performance of the investigated catalysts.

Time-of-flight secondary ion mass spectrometry (ToF-SIMS) was applied to the characterization of the surface composition of the studied catalysts Au-Ni/Al_2O_3 and Ru/C before and after reaction in the formic acid decomposition with levulinic acid hydrogenation with the use of sulphuric acid as a solvent and sodium hydroxide, which was used to increase the pH.

Then, based on the ToF-SIMS spectra, the intensity ratio of the selected ions was calculated. The results are shown in Table 4.14 and 4.15.

Table 4.14 Normalized intensity of ions calculated on the basis of ToF-SIMS spectra collected from the surface of Ni-Au/Al_2O_3 catalyst.

Ions	Before reaction	After reaction
Au^+/Ni^+	1.00×10^{-2}	1.17×10^{-2}
Ni^+/ $AlOH^+$	2.59	3.27
Au^+/ $AlOH^+$	0.026	0.039
Na^+/Au^+	12.10×10^{2}	17.01×10^{2}
Na^+/Ni^+	11.46	19.40
Na^+/ $AlOH^+$	29.71	63.60
S^-/total$^-$	0.67×10^{-3}	6.81×10^{-3}
S^-/Au^-	0.49	3.21
S^-/Ni^-	1,13	29.10
$S^-/AlOH^-$	0.56	7.59
SO_2^-/Au^-	0.29	3.70
SO_2^-/Ni^-	0.68	33.50
$SO_2^-/AlOH^-$	0.33	8.74

To better understand the surface composition of Au-Ni/Al_2O_3 catalyst, the ions which origin from metal and support were selected.

The Ni^+/Au^+ ions surface ratio showed the similar value before and after the process, meaning that the interaction of the two metals was the same or changed in the same range.

In order to analyse the changes of the metals distribution on the support the following ion rations were analysed $Ni^+/AlOH^+$ and $Au^+/AlOH^+$

By comparing those values before and after the process it is possible to conclude that their intensity slightly increased in the both cases after the reaction. Besides ions which origin from metals, it was also important to obtain information about the presence of sulphur and sodium ions on the surface of catalyst. The following ions could be adsorbed on the surface of catalyst due to the presence of sulphuric acid and sodium hydroxide in the reaction mixture. For this reason, the intensity of signal of S^-, SO_2^- and Na^+ was identified.

In the case of the presence of sodium ions in the reaction, high intensity of Na^+ signals were observed on the samples after reaction.

It was possible to identify that the amount of sodium increased on the surface of the catalysts after the reaction. Significant increase was observed both on Ni and on alumina surface which was shown by the higher value of the respective ion ratios after the reaction ($Na^+/ AlOH^+$ and Na^+/ Ni^+)

This can suggest that a large amount of sodium was deposited on the support of catalyst and on metal sites. It was also observed that S^- and SO_2^- increased the intensity after reaction, especially a huge increase was observed on the surface of Ni which means that probably considerable amount of sulphur containing species were adsorbed on this metal.

This could explain why the activity of this catalyst was very low in the reaction, because the surface of catalyst was probably blocked by adsorbed impurities preventing the occurrence of the reaction.

Table 4.15 Normalized intensity of selected ions on the basis of ToF-SIMS spectra collected from the surface of Ru/C catalyst.

Ions	Before reaction	After reaction
Ru^+/C^+	1.48	1.02
Na^+/C^+	40.4	82.02
Cl^-/C^-	0.50	0.65
S^-/C^-	4.11	4.48
SO^-/C^-	0.72×10^{-2}	1.58×10^{-2}
SO_2^-/C^-	0.58×10^{-2}	2.15×10^{-2}

In the next step the surface of Ru/C before and after reaction was also evaluated by ToF-SIMS. The chosen ions identified on the surface of the catalyst which origin both from metal, support and presence of impurities are presented in the Table 4.15.

In the case of Ru/C catalyst it was not possible to present the intensity of the relative ions as to total ions observed because of the application of silica which was used during the preparation of sample for analysis, making the catalyst diluted in it. Thus, the identified intensity of total ions can be higher than really is present on the catalyst surface.

A lower value of Ru^+/C^+ surface ratio after reaction was observed. This indicates that ruthenium nanoparticles present on the surface of catalyst probably were covered during the reaction by adsorbed impurities or carbon deposit.

Further measurements exhibited also a considerably high intensity of SO^- and SO_2^- present on the surface of investigated catalyst. That can be directly related to the absorption of sulphur containing species on the support. Similarly, the Na^+/C^+ ions ratio also presented higher value after reaction, which suggests that a large amount of sodium was adsorbed on the support as well.

In general, both samples analysed after the reaction displayed signals coming from sulphur and sodium. However, in case of Au-Ni/Al_2O_3 catalyst considerable increase (ten times

more) of the S^- and SO_2^- after the process was present in comparison to Ru/C. This can explain the lower activity in the reaction.

4.7.2 Temperature programmed reduction measurements (TPR)

In the next step of the characterization, the reducibility of Ru/C catalyst was studied by temperature programed reduction (TPR) measurements, because this catalyst showed the best activity.

The TPR measurements were performed to understand what kind of metal species are present on the catalyst surface and which kind of interaction exist between metal particles with the support in order to relate those observations to catalytic activity. It was applied before reduction (fresh catalyst) and after reaction (spent catalyst) in the simultaneous formic acid decomposition and levulinic acid hydrogenation performed in sulphuric acid and in the presence of sodium hydroxide.

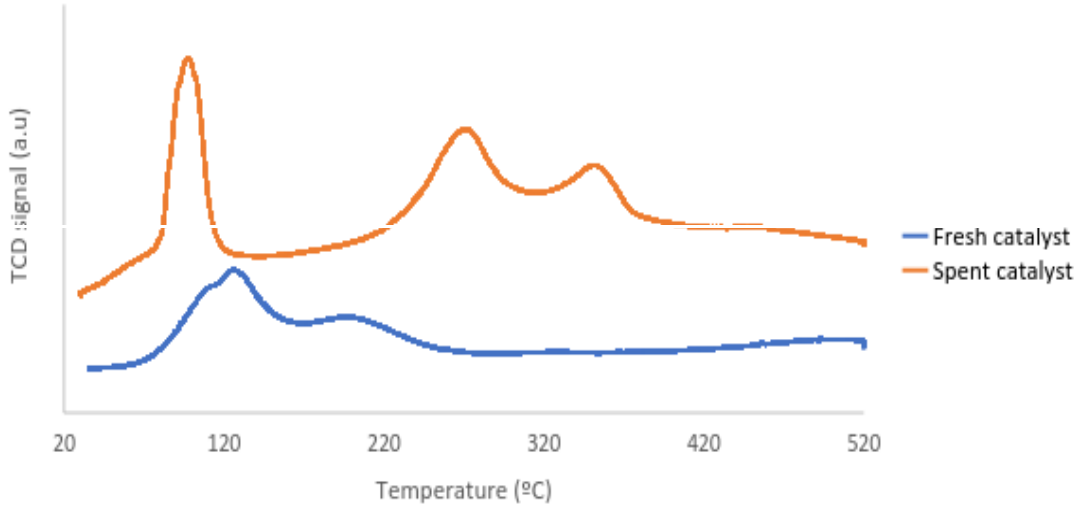

Figure 4.12 Temperature programmed reduction profiles of 5%Ru/C catalyst.

The reduction profiles presented in Figure 4.12 demonstrated several regions of H_2 consumption for the fresh and spent catalyst.

In the case of fresh catalyst, it was possible to identify two main peaks with the maximum at 129°C and 201°C. In the first main peak, it was also possible to observe, shoulder with maximum at 109ºC. These two main peaks are probably related to the two reduction steps of the ruthenium chloride precursor, i.e. $Ru^{3+} \rightarrow Ru^{2+} \rightarrow Ru^0$. Additionality, the peak with maximum at 201ºC indicates the reduction of ruthenium species, which strongly interact with support surface.

The peaks on TPR profile indicate the reduction of different nanoparticles of RuO_2 amorphous or crystalline or just of different nanoparticle sizes as well. An example of such behaviour can be also found in the literature [34].

The achieved results permit to conclude that, in the case of fresh catalyst, the minimum temperature of reduction seems to be at 200ºC, but according to the literature, reduction at 500ºC optimize the catalytic activity of Ru/C [34]. This explain why in this work the reduction was carried out at 500ºC.

In the case of spent catalyst, it was possible to observe three regions of H_2 consumption: first peak with maximum at 99ºC, second at 274ºC and third at 355ºC. The highest intensity peak (99ºC) can be connected to the reduction of ruthenium oxide species, which origin is probably from drying step.

Two next peaks are related to the reduction of species, which probably were adsorbed on the surface of the catalyst during the reaction.

When it comes to the comparison of those two catalysts it was possible to notice the presence of two additional peaks in the high temperature region which could be related with the reduction of the adsorbed molecules. This is in accordance with ToF-SIMS results as well.

5

Conclusions

In this work, the catalytic performance of ruthenium supported on carbon in the hydrolytic hydrogenation of biomass was investigated.

Four types of wood such as: pine, birch, poplar and beech were selected as biomass feedstock and several parameters of biomass hydrolysis towards levulinic acid (LA) and subsequent hydrogenation towards γ-valerolactone (GVL) were discussed.

Based on the analysis of the results, the different composition of the wood samples was identified.

The highest amount of cellulose (52%) was showed in the case of poplar wood, followed by pine (51%), beech (47%) and finally birch (45%).

The results of the X-ray diffraction (XRD) analysis revealed the difference of the crystallinity degree between the investigated biomass samples, it can be related with their composition.

In general, the sample which presented a higher amount of cellulose showed a high crystallinity index.

Fourier Transform Infrared Spectroscopy (FTIR) analysis allowed to identify the differences in the structure of wood samples and cellulose.

Due to the high content of cellulose, many similar groups were identified in both types of the materials. More bands were however identified in the case of wood samples, which origin from different functional groups present in lignin and hemicellulose.

The acidic hydrolysis of wood samples resulted in the formation of levulinic acid and formic acid. Their amount and their ratio were different for the different types of wood.

The results of the catalytic tests of the hydrogenation of levulinic acid with formic acid used as hydrogen source revealed that this reaction depends on several factors.

Firstly, it was identified that reaction is influenced by the pH of the solution. A lower pH has a stronger influence on the formic acid decomposition than on the levulinic acid hydrogenation.

Therefore, the hydrolytic mixture needs to be firstly neutralized before it can be hydrogenated towards γ-valerolactone. The highest γ-valerolactone yield was obtained when NaOH was used for neutralizing the hydrolytic mixture. Secondly, hydrolytic hydrogenation depends on the catalysts that was used for this process.

Among three tested catalysts 4% Ni-Au/Al_2O_3, 5%Ru/10%Ca-TiO_2 and 5% Ru/C, the highest γ-valerolactone yield was found for ruthenium supported on carbon (41%).

For hydrogenation reactions performed directly from lignocellulosic biomass, high conversion of levulinic acid and formic acid was observed however no γ-valerolactone was noted.

Time-of-flight secondary ion mass spectrometry proved to be a technique of choice in the analysis of the catalyst surface. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) revealed that ruthenium nanoparticles present on the surface were covered by adsorbed impurities during the reaction (mainly Na^+ and S^-) or carbon deposit.

The presence of those species on the catalyst surface could strongly influence the catalytic activity. This was related to the presence of other components and impurities in the reaction mixture.

Those observations were confirmed by Temperature Programmed Reduction (TPR), and on the spent catalyst, the presence of the adsorbed molecules was identified.

In this work, several important factors that have an influence on the catalytic hydrolytic hydrogenation of lignocellulosic biomass were identified. This topic is however very broad and

therefore, more other parameters need to be checked to improve the efficiency of lignocellulosic valorisation.

6

Perspectives

Biomass has received considerable attention as a sustainable feedstock that can replace diminishing fossil fuels for the production of chemicals, fuels and materials. However, one of the main challenges in the utilization of lignocellulosic biomass is pretreatment and hydrolysis for the production of sugars, and these steps are considered the greatest impediment to economic viability of strategies involving the production of sugars from lignocellulosic biomass. γ-Valerolactone (GVL) is considered a platform molecule for conversion to many useful chemicals. Moreover, only few studies reports synthesize of γ-valerolactone (GVL) directly from biomass, most research pertaining to LA hydrogenation to produce GVL has employed pure, commercial LA or mixtures of commercial compounds that simulate the products that would be obtained from the hydrolysis of cellulose or lignocellulosic biomass.

This thesis shows ruthenium catalyst as a potential catalyst in levulinic acid hydrogenation with formic acid as an internal hydrogen source. However, in the hydrolytic hydrogenation of biomass lower activity was observed. Therefore, among several results some of them required more detailed analysis and future study. As such, the catalysis research should focus on (a)better understanding the influence of impurities or other compounds origin from lignocellulosic materials; (b) improving facile strategies to remove or neutralize sulphate into the solution, (c) methods for the synergistic coupling of hydrolytic and thermochemical methods into a fully integrated biorefinery,(d) others types of lignocellulosic biomass because hydrolytic strategies are not well suited to all type of biomass, particularly those containing large fraction of lignin.

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Appendix

A appendix: JCPDS of cellulose

Name and formula

Reference code:	00-003-0289
Compound name:	Native cellulose
PDF index name:	Native cellulose
Chemical formula:	$(C_6H_{12}O_6)_x$

Crystallographic parameters

Crystal system:	Monoclinic
a (A):	8,3500
b (A):	10,2800
c (A):	7,9600
Alpha (°):	90,0000
Beta (°):	102,0000
Gamma (°):	90,0000
Measured density (g/cm^3):	1,60
Volume of cell (10^6 pm^3):	668,34
RIR:	-

Comments

Creation Date: 1970-01-01

Modification Date: 1970-01-01

Volume of the unit cell = 668A@3. Reflections obtained from fiber diagram with uncertainty in intensity ratios. (Ed.). Reason O Quality Was Assigned: O assigned because average D2□ is 0.058.

References

Primary reference: Andress., *Z. Phys. Chem. (Leipzig)*, **136**, 279, (1928)

Peak list

No.	h	k	l	d [A]	2Theta[deg]	I [%]
1	-1	0	1	6,28000	14,091	20,0
2				5,94000	14,902	80,0
3	-1	1	1	5,37000	16,494	70,0
4	1	0	1	5,11000	17,340	20,0
5	0	2	1	4,30000	20,639	60,0
6	0	0	2	3,89000	22,842	100,0
7	1	3	0	3,16000	28,218	40,0
8	-1	2	2	3,07000	29,063	40,0
9				2,94000	30,378	40,0
10	1	3	1	2,86000	31,249	40,0
11	3	1	0	2,63000	34,062	60,0
12	-2	3	1	2,59000	34,605	40,0
13	0	4	0	2,57000	34,882	80,0
14	-2	3	2	2,33000	38,610	40,0
15	2	4	0	2,17000	41,584	60,0
16	1	2	3	2,12000	42,612	20,0
17	3	0	2	2,04000	44,370	20,0
18	-4	1	2	1,95000	46,535	40,0

Stick Pattern